FINNISH INSTITUTE OF MARINE RESEARCH – CONTRIBUTIONS

No. 17

Kaarina Lukkari

Chemical characteristics and behaviour of sediment phosphorus in the northeastern Baltic Sea

Finnish Institute of Marine Research, Finland
Helsinki 2008

It is the mark of an educated mind to rest satisfied with the degree of precision which the nature of the subject admits, and not to seek exactness where only an approximation is possible.

Aristotle

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ISSN 1457-6805
ISBN 978-951-53-3134-2 (Paperback)
ISBN 978-952-10-5125-8 (PDF)

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Academic dissertation in Environmental Soil Science to be presented, with the permission of the Faculty of Agriculture and Forestry of the University of Helsinki, for public examination in Auditorium XII, University of Helsinki, Unioninkatu 34, Helsinki, on December 18th, 2008, at 12 o'clock noon.

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LIST OF ORIGINAL ARTICLES

This thesis is based on the following papers, which are referred to in the text by their Roman numerals:

I Lukkari, K., Hartikainen H. and Leivuori, M. 2007. Fractionation of sediment phosphorus revisited: I Fractionation steps and their biogeochemical basis. Limnology and Oceanography: Methods, 5: 433–444.

II Lukkari, K., Leivuori, M., and Hartikainen H. 2007. Fractionation of sediment phosphorus revisited: II Changes in phosphorus fractions during sampling and storing in the presence or absence of oxygen. Limnology and Oceanography: Methods, 5: 445–456.

III Lukkari, K., Leivuori, M., and Hartikainen, H. 2008. Vertical distribution and chemical character of sediment phosphorus in two shallow estuaries in the Baltic Sea. Biogeochemistry, 90: 171–191.

IV Lukkari, K., Leivuori, M., and Kotilainen, A. Trends in chemical character and burial of sediment phosphorus from open sea to organic rich inner bay in the Baltic Sea. Biogeochemistry (under revision).

V Lukkari, K., Leivuori, M., Vallius, H., and Kotilainen, A. The chemical character and burial of phosphorus in shallow coastal sediments in the northeastern Baltic Sea. Biogeochemistry (under revision).

THE AUTHORS' CONTRIBUTION TO THE ARTICLES

I Lukkari designed and executed the study, analysed the data, interpreted the results, and wrote the manuscript. Prof. Helinä Hartikainen contributed with conclusions and comments. Dr. Mirja Leivuori contributed with comments.

II Lukkari designed and executed the study, analysed the data, interpreted the results, and wrote the manuscript. Prof. Helinä Hartikainen contributed with conclusions and comments. Dr. Mirja Leivuori contributed with comments.

III Lukkari participated in designing the study (with participants of the SEGUE consortium), data collection and analysis, interpreted the results, and wrote the manuscript. Prof. Helinä Hartikainen contributed with conclusions and comments. Dr. Mirja Leivuori participated in designing the study, data collection, analysis, and comments.

IV Lukkari designed the study, participated in data collection and analysis, interpreted the results, and wrote the manuscript. Dr. Mirja Leivuori participated in designing the study, data collection, analysis, and comments. Prof. Aarno Kotilainen made sediment descriptions, wrote the geological description of the sampling area, and contributed with comments.

V Lukkari designed the study, participated in data collection, and analysis, interpreted the results, and wrote the manuscript. Dr. Mirja Leivuori participated in designing the study, data collection, analysis, and comments. Dr. Henry Vallius provided part of the data and, together with Prof. Aarno Kotilainen, made sediment descriptions and contributed with comments. Prof. Aarno Kotilainen wrote the geological description of the sampling area.

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Lukkari, K. 2008: Chemical characteristics and behaviour of sediment phosphorus in the northeastern Baltic Sea. Finnish Institute of Marine Research – Contributions No. 17, 2008.

ABSTRACT

Eutrophication is a severe environmental problem in the Baltic Sea, especially in the Gulf of Finland and the Archipelago Sea, and it is enhanced by the release of phosphorus (P) from bottom sediments. The release of P from sediment reserves largely depends on the occurrence of P in different chemical forms and on the prevailing conditions, especially on the presence of oxygen. This study examines the chemical character and the vertical distribution of sediment P in two shallow estuaries, in shallow coastal sediments overlain by oxic near-bottom water, and in poorly oxygenated open sea sediments in the northeastern Baltic Sea. The objective was to evaluate how much of the sediment P is buried and removed from the nutrient cycle, and how much of it is in forms that can be released from the sediment to the overlaying water over time. Relationships between the distribution of the different P forms and the chemical and physical properties of the sediment, sediment pore water, and near-bottom water were determined in order to examine the behaviour of P at the sediment-water interface.

The results show that the chemical character of sediment P varied in the different areas. Generally, in the outer estuaries and in the organic-rich coastal areas in the eastern Gulf of Finland, the sediments were higher in P than the sediments in the poorly oxygenated open sea areas in the central and western Gulf. The estuary sediments that received erosion-transported material were characterised by P bound to hydrated oxides of iron and aluminum. Iron-bound P is sensitive to changes in redox-conditions, but part of it was buried in the estuaries, possibly because of high sedimentation rates and incomplete reduction of iron. The open sea sediments in the central and western Gulf of Finland were dominated by apatite-P, which was also abundant in the areas strongly affected by sediment transportation. The burial of sediment P was most effective in the areas rich in apatite-P, which is a relatively stable form of P in sediment. In the eastern Gulf of Finland, organic P forms predominated in the organic-rich sediments. A part of these P forms will be buried, while part will be degraded in the long term, releasing soluble P to the pore water. In the poorly oxygenated areas, iron compounds at the sediment surface are not able to retain P released during mineralisation of organic matter or reduction-induced dissolution of iron-compounds in deep sediment layers. However, in the shallow coastal areas overlain by oxic near-bottom water, the organic-rich surface sediment can also become temporarily reduced and release P from the sediment to the overlaying water. The considerable variation in the chemical composition of sediment P reserves in the northeastern Baltic Sea proved that it is an important factor and should be taken into account when evaluating the release of sediment P and the role of P reserves in bottom sediments in eutrophication.

Key words: Baltic Sea, fractionation, phosphorus, sediment

1. INTRODUCTION

1.1 Specific features of the Baltic Sea and contribution of sediment P to eutrophication

The Baltic Sea (BS) is a large brackish water basin (surface area 415 000 km^2; HELCOM 2007). It formed after deglaciation of the BS basin between approximately 15 000 and 10 000 years B.P. The various phases of the BS, Baltic Ice-Lake, Yoldia Sea, Ancylus Lake, and Litorina Sea (and Limnea Sea) differed in their connections to the ocean and, thus, in salinity and occurrence of different species. The present brackish water basin formed about 3000 B.P., when the uplifting of land narrowed the connection of the Litorina Sea to the North Sea through the Danish Straits, and the salinity decreased. The basin is still changing as uplift continues, mostly in the northern BS (Winterhalter & al. 1981). Because of its large drainage area (1 740 000 km^2; HELCOM 2007), the BS receives large amounts of fresh water. In contrast, high salinity water flows in from the North Sea through the Danish Straits and creates strong salinity stratification in the Baltic Proper (BP). The halocline lies at about 60–80 m depth and restricts mixing of the bottom water (10–13 PSU) with well-oxygenated surface water, often resulting in oxygen (O_2) depletion at the bottom. If the meteorological conditions are correct, strong saline water pulses can renew and oxygenate the bottom water in the BP (Kullenberg 1981).

The Gulf of Finland (GoF), in the northeastern BS, is topographically a continuation of the BP and exchanges water with the main basin (Winterhalter & al. 1981). If water intrusion through the Danish Straits is not strong enough, well-oxygenated water does not reach the GoF; instead, the GoF receives poorly oxygenated near-bottom water from the BP. Sediments in the GoF are high in organic matter (OM), which is transported to the Gulf by drainage water and river discharge or is produced within the ecosystem, driven by high nutrient loading (Carman 1998, Carman & Cederwall 2001, Grimvall & Stålnacke 2001, HELCOM 2004). Microbial degradation of organic matter (OM) consumes O_2 from the sediment-water interface and, if salinity (or temperature) stratification prohibits efficient vertical mixing, the near-bottom water in the GoF turns hypoxic (concentration of dissolved O_2 <2.0 ml l^{-1}; Conley & al. 2002) or anoxic. Since the mid 1990s, the GoF has frequently suffered from poor O_2 conditions (HELCOM 2003, Laine & al. 2007, Olsonen 2007).

The specific features of the BS, its semi-enclosed nature, brackish water, salinity stratification, partial ice cover in winter, and large drainage area make the BS ecosystem particularly vulnerable to various environmental stresses (Dybern & Fonselius 1981, HELCOM 2003). One of the major concerns is eutrophication, i.e., increased biological production due to excess nutrients (Larsson & al. 1985, Bonsdorff & al. 1997, HELCOM 2002, 2003). Extensive algal blooms, especially those of cyanobacteria, are harmful symptoms of eutrophication and restrict the recreational and economic use of the sea. Nitrogen (N_2) fixing cyanobacteria, some of which are toxic, particularly benefit from excess phosphorus (P) (Hällfors & al. 1981). This makes P a key element in the eutrophication of the Baltic.

High population and intensive agriculture in the large drainage area has caused severe nutrient loading to the BS since the mid 20^{th} century. It has been estimated that P loading to the BS is about 8-fold higher than it was at the beginning of the century (Larsson & al. 1985). However, poor O_2 conditions and cyanobacteria blooms also sometimes occurred in the BS before increased anthropogenic loading of P, ever since the beginning of the brackish water Litorina Sea phase (Bianchi & al. 2000, Finni & al. 2001). Although hypoxia and cyanobacteria could be, to some extent, considered natural for the BS, the algal blooms are more frequent and they extent to larger sea areas than several decades ago (Kahru & al. 1994, Kononen & Niemi 1984). Thus, the impact of human activities on P loading in the Baltic seems evident and results (along with changes in salinity), for example, in increased areas of hypoxic bottom sediments (Persson & Jonsson 2000, Conley & al. 2002). Despite attempts to decrease P loading to the BS, the results have been insufficient. In 2000, loading of P (from rivers, coastal areas, and point sources) to the entire Baltic was about 34 600 t and to the GoF about 6030 t (HELCOM 2004). The P loading is mostly caused by diffuse and point sources of anthropogenic origin, e.g. agriculture, municipal and industrial wastewaters, and fish farming (HELCOM 2003). In the GoF, which is one of the most heavily loaded and most severely eutrophied areas of the BS, P loading has decreased over the past two decades (Pitkänen & al. 2001, Kiirikki & al. 2003). Despite that, eutrophication and the occurrence of algal blooms have not diminished, and long-term measurements of wintertime phosphate (PO_4-P) concentrations in water reveal an increasing trend over the past ca. twenty years (Olsonen 2007, Suikkanen & al. 2007, Fleming-Lehtinen & al. 2008). Evidently, anthropogenic P loading has not decreased enough, but there is also another reason for elevated P levels: release of P from the bottom sediments, in which it has accumulated for decades (Emeis & al. 2000, Pitkänen & al. 2001).

Nutrient loading increases productivity and, consequently, the amount of OM deposited in bottom sediments (Larsson & al. 1985, Jonsson & Carman 1994). A large amount of the P in seawaters is removed by OM (Berner & al. 1993), thus, a con-

siderable part of P reaching the sea floor is in organic form. In estuaries and near shore areas, however, the transportation of terrestrial inorganic P, e.g., in mineral lattices (apatite-P) and bound on the surfaces of metal oxides, is high and contributes to the P deposition. The most easily degradable part of OM is mineralised during transportation in the water column and settling to the sea floor but, especially in shallow areas, a part of it reaches the bottom sediments (Fisher & al. 1982, Froelich & al. 1982). Microbial degradation of OM continues at the sediment-water interface and in the sediment and consumes O_2. If the near-bottom water is not mixed with oxic water, O_2 consumption can lead to hypoxia, or anoxia, and destroy benthic fauna (Larsson & al. 1985). In addition, O_2 depletion has a strong impact on P cycling (Fig. 1). In reducing conditions, iron is reduced from the ferric form (Fe^{3+}) to the ferrous form (Fe^{2+}), and poorly crystallised Fe-oxyhydroxides that bind P efficiently are dissolved and release P bound by Fe oxide (Einsele 1936, 1938, Mortimer 1941, 1942). Fe^{3+} is reduced microbially or chemically (Canfield 1989, Burdige 1993), directly (Lovley & Phillips 1986a) or via sulphide production by sulphate-reducing bacteria (Berner 1970). According to the sequence of redox reactions in marine sediments (Froelich & al. 1979, Burdige 1993), in addition to O_2, Fe^{2+} can also be oxidised in the sediment by NO_3^- (coupled to dissimilatory NO_3^- reduction; e.g., Straub & al. 1996) and Mn oxides. If the sediment surface is oxidised, dissolved Fe, diffusing upwards in the pore water, will oxidise again and form new ferric oxyhydroxides that are able to capture upwards-diffusing PO_4-P (Mortimer 1971, Boström & al. 1982, Sundby & al. 1992). The presence of sulphide in reduced sediments, however, binds Fe^{2+} through formation of ferro-sulphides and pyrite (FeS_2), resulting in a decrease in the P sorption capacity of the oxidised surface layer (Berner 1970, Caraco & al. 1989, Krom & Berner 1980, Roden & Edmonds 1997, Anschutz & al. 1998).

If the reduction- or mineralisation-released PO_4-P in pore water is not bound to Fe oxyhydroxides or other sorption surfaces, precipitated (e.g., with Ca), or incorporated into benthic organisms, it can diffuse to the near-bottom water of lower PO_4-P concentration (Froelich & al. 1982). In addition, the burrowing activity of benthic animals can mix P-rich pore water with the near-bottom water (Aller 1988) or result in upward mixing of sediment particles and consequent desorption of PO_4-P sorbed onto particle surfaces (Schink & Guinasso 1978, Slomp & al. 1998). Part of the PO_4-P can be bound to suspended particles in the oxidised water layer, but when the P-rich near-bottom water is mixed with the productive layer, especially during upwelling events (Haapala 1994, Vahtera & al. 2005), P released from sediments enhances biological productivity and eutrophication. Thus, excess nutrients cause a "vicious circle" through increased production and degradation of OM, O_2 depletion, and internal P loading, i.e., eutrophication fuels itself via the P reserves in the bottom sediments (Dybern & Fonselius 1981, Vahtera & al. 2007). The chemical character of the P reserves affects the potential for their release from sediments (Williams & Mayer 1972). In addition to Fe-bound P, some other forms of sediment P can act as sources of P for the water column. In contrast, some P forms occur in mineral structures or are strongly bound on particle surfaces and will be buried with sediment and removed from the nutrient cycle. Therefore, in addition to the amount of P reserves in the bottom sediments, it is important to know their chemical character in order to understand the potential role of sediment P as a P source and its impact on eutrophication in the BS.

1.2 Occurrence of P in Baltic Sea sediments

The average concentration of PO_4-P in ocean waters is about 2.3 μmol l^{-1} (Gulbrandsen & Roberson 1973). Warm surface waters are estimated to contain about 0.3 μmol l^{-1} (or less) P, while deep and cold waters may contain nearly 10 μmol l^{-1} PO_4-P (McKelvey 1973, Gulbrandsen & Roberson 1973). In the BS, the range for water column PO_4-P concentration varies from close to zero to 9 μmol l^{-1}. The highest values occur in the deepest water layers during hypoxic conditions and the lowest concentrations in the surface waters during high production and consumption of nutrients (Grasshoff & Voipio 1981).

Generally, P forms 0.13 % of basaltic rocks in the oceanic crust, and 0.04% and 0.13% or more of deep-sea carbonate sediments and deep-sea clays, respectively. The P-rich marine deposits, phosphorites, formed in upwelling areas of high productivity, can contain up to 13% P (McKelvey 1973). In the BS, the sediment P concentration has been reported to vary considerably, from 0.02% to 0.46%, the highest percentages occurring in the surface sediment in the Gotland Deep after positive redox-turnover (Winterhalter & al. 1981). In the Bothnian Sea, oxic sediments are enriched with Fe, which effectively traps P (0.17%, on average; Niemistö & al. 1978). In addition, in some areas of the BS, e.g., in the Gulf of Riga (GR), eastern GoF, and the Bothnian Bay (BB), P is enriched (up to 1.65%) in Fe and manganese (Mn) rich nodules in the surface sediment (Winterhalter & al. 1981, Zhamoida & al. 2007). Excluding P-rich nodules, high sediment P concentrations have been reported in oxic surface sediments in the eastern GoF (about 175 μmol g^{-1}, i.e., ca. 0.56%; Carman 1998) and northeastern GoF (117 μmol g^{-1}; Conley & al. 1997), in the Gdansk Bay (about 130 μmol g^{-1}; Carman 1998), and in the

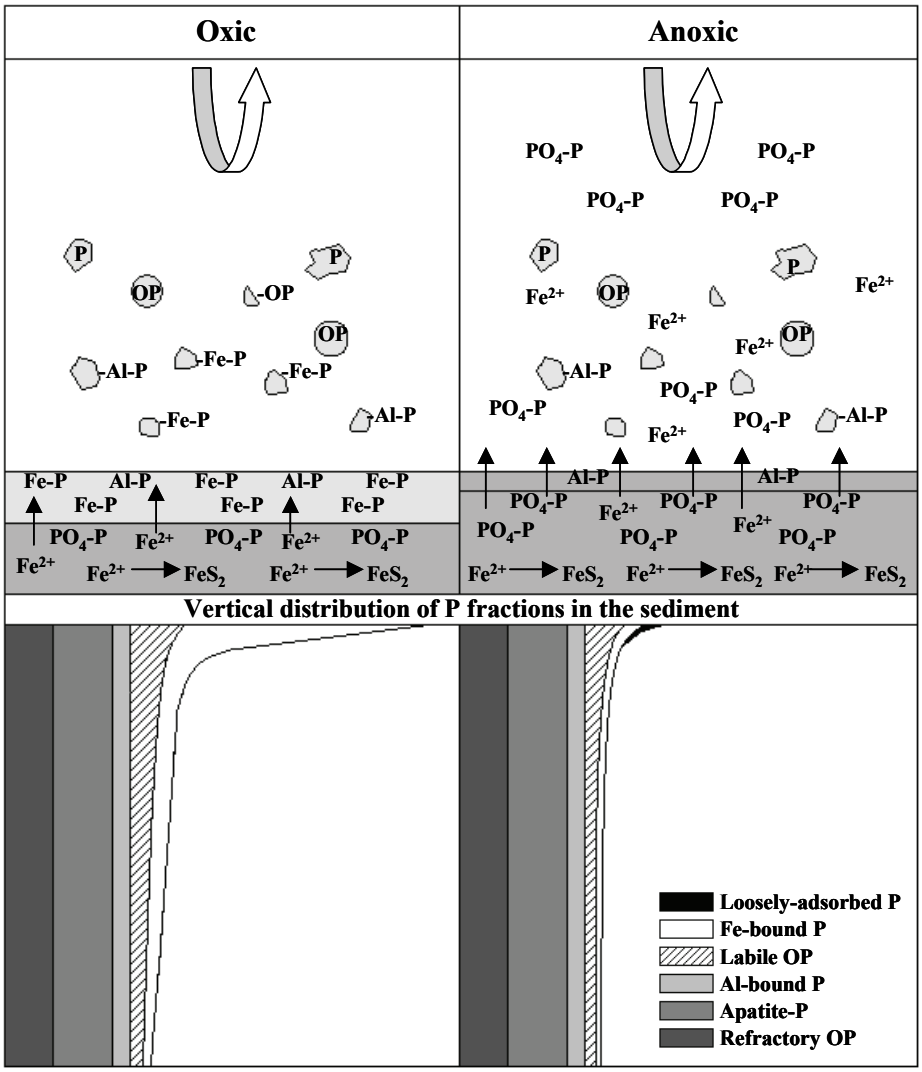


Fig. 1. Schematic overview of the behaviour of P and its chemical binding and solubility forms at the sediment-water interface.

Bothnian Sea (ca. 100 µmol g^{-1}; Carman 1998, Lukkari, unpublished data). In contrast, relatively low sediment P concentrations are found in Kattegat, southeastern GoF (ca. 20–30 µmol g^{-1}; Carman 1998), in the BP (ca. 30 µmol g^{-1}, Carman & Rahm 1997) as well as in sandy sediments in the GR (ca. 10 µmol g^{-1}; Carman & al. 1996) and in the Kiel Bight (ca. 8 µmol g^{-1}; Balzer 1986). Carman and Cederwall (2001) compared different bottom types in the BS, and the average concentrations of P (in surface sediments of the BP, Bothnian Sea, BB, GoF, and GR) were about 52, 38, and 24 µmol g^{-1} in accumulation, transportation, and erosion bottoms, respectively.

Concentrations of P in the sediment pore water can be a few hundred times higher than in the near-bottom water. The lowest (<1 µmol l^{-1}) PO_4-P concentrations are generally found in oxic surface layers where Fe oxyhydroxides trap PO_4-P diffused from the deeper layers (Mortimer 1971, Slomp & al. 1996a, Carman & Rahm 1997). In contrast, the highest values are found in deep, anoxic sediment layers. For example, in the BS, PO_4-P concentrations of about 250 µmol l^{-1} have been reported in the central GoF (Conley & al. 1997) and in the central (Matthiesen & al. 1998) and southern (Carman & Rahm 1997) BP. In the western BP, Matthiesen et al. (1998) recorded pore water PO_4-P concentrations of up to ca. 700 µmol l^{-1}.

1.3 Chemistry and binding properties of P

Phosphorus is an essential element for life. It is a macronutrient and a constituent of vital molecules, e.g., those carrying chemical energy (adenosine triphosphate, ATP, and adenosine diphosphate, ADP) and genetic information (deoxyribonucleic acid, DNA, and ribonucleic acid, RNA) in cells. In addition, it is a structural constituent of, for example, cell membranes (phospholipids), bones, and teeth (hydroxyapatite). Thus, P can be found everywhere

that living or dead organisms are present. Furthermore, as the eleventh most abundant element in igneous rocks, P is a constituent of many minerals, and P forms about 0.1% of most rocks in the earth's crust (Golterman 1973, McKelvey 1973). Phosphorus has five electrons in the outer shell of the atom and, in general, it occurs in the pentavalent positive state (although the trivalent negative state is possible; Van Wazer 1973, Glindemann & al. 2005) and is not affected by redox conditions, except via its compounds (McKelvey 1973). Phosphorus forms covalent bonds with neighbouring atoms. It readily forms phosphates with oxygen, and the four negatively charged oxygen atoms make the anion reactive, so that it interacts with many inorganic and organic solid phases (Van Wazer 1973, Bohn & al. 1985). The orthophosphate (ortho-P) anion (i.e., PO_4-P) exists in aquatic systems mainly as HPO_4^{2-} and partly as $H_2PO_4^-$ anions, which can be complexed with cations in seawater (Gulbrandsen & Roberson 1973, Atlas & al. 1976, Stumm & Morgan 1996).

Ortho-P and pyrophosphate, which is a molecule formed of two ortho-P groups, are commonly degradation products of other P-containing molecules. Polyphosphates, molecules containing several phosphate groups, are synthesised by some microbes as storage compounds (Hooper 1973, Hupfer & al. 1995), preferentially in oxic conditions (Gächter & al. 1988, Uhlmann & al. 1990). Inorganic P can be bound to OM via metal cations, such as Al^{3+} and Fe^{3+} (Schnitzer 1969, Steinberg & Muenster 1985). According to Ingall et al. (1990), Carman et al. (2000), and Ahlgren (2006), among the most common OP groups in lake and marine sediments are orthophosphate monoesters, especially inositol phosphates (e.g., inositol-hexaphosphate, phytate; De Groot & Golterman 1993), and ortho-P diesters, such as phospholipids and (bacterial) DNA and RNA. Ortho-P diesters also include teichoic acids, which are structural compounds of some bacteria found in P-rich sediments (Ahlgren 2006). Phosphonates, containing a strong direct bond between the P and carbon (C) atoms, are found in many sediments, and they are considered resistant to acid and base hydrolysis and possibly also to microbial degradation (Van Wazer 1973, Ingall & al. 1990, Clark & al. 1998, Carman & al. 2000). However, some marine organisms may be able to use them as a nutrient source in anoxic conditions (Benitez-Nelson & al. 2004, Dyhrman & al. 2006). The most unstable and easily degradable molecules of OM (for example, phosphosaccharides like ATP) are degraded already in the water column, and the OM deposited to the sediment and finally buried is enriched with C (Froelich & al. 1982, Berner & al. 1993) and contains more refractory OP molecules, e.g. phosphonates (Clark & al. 1998), or P incorporated into complex molecules of humic matter (Celi & Barberis 2005). The availability of OP for bacteria and algae depends on the stability of the molecules against enzymatic (or chemical; Baldwin & al. 2005) hydrolysis in microbial degradation (Quiquampoix & Mousain 2005), and microbial activity depends on temperature and availability of electron acceptors and other nutrients. In addition, the availability of OP for microbial degradation depends on associations of OP on mineral surfaces. For example, in oxic conditions, binding of OP onto metal oxide surfaces via PO_4-P groups retards their mineralisation (Bohn & al. 1985, Ognalaga & al. 1994, Suzumura & Kamatani 1995, Celi & al. 1999, Celi & Barberis 2005). When OP is remineralised and recycled during biogeochemical processes in sediment, part of it will always be transformed into refractory forms and buried. The burial of OP has been shown to be more efficient in oxic conditions than burial of organic C, resulting in low organic C/P ratios (Ingall & al. 1993, Ingall & Jahnke 1994, 1997, Schenau & De Lange 2001, Slomp & al. 2002, Virtasalo & al. 2005). The mechanism for this phenomenon is still unclear but it has been explained, for example, by more efficient storage of P in bacterial cells in oxic than in anoxic conditions (Ingall & al. 1993, Van Cappellen & Ingall 1994). Finally, refractory OP is transformed into authigenic minerals in sediments (i.e., sink-switching; Froelich & al. 1982, Ruttenberg & Berner 1993, Delaney 1998).

1.3.1 Phosphorus in common sediment minerals and on particle surfaces

Apatite ($Ca_5(PO_4,CO_3)_3(F,Cl,OH)$) is one of the most abundant P-containing minerals in soils and in marine sediments (McKelvey 1973). Relatively inert detrital apatite is transported to the sea from the terrestrial environment as a result of rock weathering and erosion, while authigenic apatite minerals, e.g. carbonate-fluorapatite, are formed in marine sediments (Ruttenberg 1992). Hydroxyapatite is a common mineral and fluorapatite is an important constituent of phosphorites, sedimentary rocks, and especially igneous rocks. Other P minerals found in aquatic sediments are for example variscite ($AlPO_4 \cdot 2H_2O$), strengite ($FePO_4 \cdot 2H_2O$), vivianite ($Fe_3P_2O_8 \cdot 8H_2O$), brushite ($CaHPO_2 \cdot 2H_2O$), wavellite ($Al_3(OH)_3(PO_4)_2 \cdot 5H_2O$), anapaite ($Ca_3Fe(PO_4)_3 \cdot 4H_2O$), octocalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 3H_2O$) and other calcium phosphates of varying solubilities (Leckie 1969, Altschuler 1973, Nriagu & Dell 1974, Psenner & al. 1984, Pettersson & al. 1988). Part of the sediment P is bound to clay minerals, to metal oxide groups at their lattice edges and to metal oxide coatings. Depending on pH, concentrations of other elements, and redox conditions, P released from Fe-oxyhydroxides or in mineralisation can occur in sediment pore water in dissolved forms or in small inorganic or organic

molecules. If the concentration is high enough, PO_4-P may precipitate, e.g., with Ca, forming carbonate fluorapatite, or with Fe, forming vivianite when the sulphide concentration is not too high (Berner 1980, Ruttenberg 1992).

Theoretically, phosphate anions could be bound to positively charged sorption surfaces by electrostatic attraction, e.g., on edges of some clay mineral lattices, or on Fe and Al oxyhydroxides in acidic conditions (White 1980), or with metal cations complexed in organic molecules (Schnitzer 1969, Gerke & Hermann 1992). However, the main binding mechanism for PO_4-P is a specific ligand exchange reaction, formerly known as chemisorption (White 1980). Clay minerals often have a negatively charged surface as a result of isomorphic replacement of the central cation of the Si-tetrahedra or aluminium (Al) octahedra with metal cations of lower valence, which causes repulsion of anionic species (Bohn & al. 1985). In a ligand exchange reaction, a PO_4-P anion penetrates into the coordination sphere of the central cation, for example Al^{3+} or Fe^{3+}, and binds to the metal cation via its own O-atom, replacing the hydroxyl (OH^-) or water (H_2O) ligand (Hingston & al. 1967, 1972, 1974, White 1980). This reaction is considered to involve two steps (Barrow 1983, Bohn & al. 1985). In the first, faster step (from minutes to hours), PO_4-P replaces the other ligand and in the second, slower step (from days to weeks), PO_4-P is moving into the inner parts of the oxide structure. In fact, this latter step may involve partial mineral dissolution and precipitation.

Suitable sorption sites for PO_4-P are metal oxyhydroxides and oxide coatings, e.g., on clay particles, as well as oxyhydroxides on lattice edges of layer silicates (Bohn & al. 1985). The most effective P binding compounds are amorphous or poorly crystallised (i.e., short-range order) oxides of Fe and Al. The molecular structure of these compounds is not as well organised as in well-crystallised oxides, and they have a larger surface area, leading to more sorption sites for P (Parfitt & al. 1975, McLaughlin & al. 1981). If the oxide surfaces are not occupied, the first PO_4-P molecules can be bound by stronger binuclear (bound to two metal cations) or bidentate (two bonds with one metal cation) binding. If, however, sorption surfaces are highly occupied already, only weaker, monodentate binding (i.e., a single coordinate bond) may be possible, and PO_4-P can be more easily replaced and removed from the oxide surface. However, these binding patterns may change depending on the P concentration in the surrounding solution and sorption and desorption processes (Hingston & al. 1974, Parfitt & al. 1975). Anions capable of competing with PO_4-P for sorption sites and replacing it are those of other weak inorganic or organic acids, which in natural aquatic systems mainly consist of OH^-, silicate ($H_3SiO_4^-$), and anions of organic acids (Scheffer & Scheffer 1984, Ryden & al. 1987). Thus, an increase in pH, i.e., an increase in OH^- concentration, favours the release of PO_4-P from sorption sites (Hingston & al. 1967). In marine systems, this is possible if, for example, surface sediment is resuspended and mixed into a water column with higher pH (Drake & Heaney 1987, Koski-Vähälä & Hartikainen 2001).

In addition, at elevated pH, the silicate anion (SiO_4-Si) competes more effectively with PO_4-P than at lower pH, because its pK_a value is higher than that of HPO_4^{2-}. Hingston et al. (1967) showed that anions of weak acids have their sorption maximum on oxide surfaces near their pK_a values. In addition to affecting PO_4-P binding on oxide surfaces and changing the surface charge of non-specific sorption surfaces, pH has a significant impact on solubility of metal phosphates and apatite (White 1980, Bohn & al. 1985). Ca-bound and apatite-P are dissolved in acid conditions, and various Ca-phosphates start precipitating at around pH 8 and higher. In contrast, Fe- and Al-phosphates form in slightly acidic conditions and have their minimum solubility around pH 6, increasing towards more acidic or alkaline conditions (Stumm & Morgan 1996). Accordingly, lower pH favours the occurrence of P with Al and Fe (preferentially bound to their hydrated oxides), whilst higher pH favours associations with Ca (White 1980, Bohn & al. 1985).

Phosphorus occurring as a structural constituent in well-organised minerals is relatively inert in soils and sediments, but biogeochemical and physical transformation processes release P as available (mainly PO_4-P) forms from other P compounds. In soils, binding of P onto oxide surfaces is fairly strong, especially at relatively low pH, typical of e.g. Finnish clayey soils, because H_2O groups are more easily replaced on metal oxide surfaces in ligand exchange reactions than OH^- groups (Hingston & al. 1972). In fact, terrestrial plants may have difficulties getting enough P, unless the pH is elevated by liming. The problem that the effective binding onto soil particles reduces the availability of soil P to plants is often solved by P fertilisation (Hartikainen 1979). However, P in fertilisers can be sorbed onto Fe- and Al-oxides in acid soils and precipitated as apatitic compounds in Ca-rich soils (Bohn & al. 1985). This may result in accumulation of P on the surface of cultivated fields. Fine particulate material is continuously eroded from soil surfaces and transported by water or wind into lakes and rivers and, finally, into the sea. Small, sheet-shaped clay particles and light organic molecules settle slowly in water and, therefore, P bound to them may be transported far before settling down in calm sedimentation environments (Postma 1967). In estuaries, however, deposition of particulate material is enhanced because of increasing salinity enhancing flocculation of suspended solids (Postma 1967, Eckert &

Sholkovitz 1976, Sholkovitz 1976, Forsgren & Jansson 1992).

In natural conditions, transportation of P from the terrestrial to the aquatic environment is restricted because of the stability of apatite minerals and the tendency of P to bind to particle surfaces. Transportation of P depends on e.g. soil properties (soil texture, amount of sorption components, and OM), precipitation and its intensity, and slope of the field. Because of anthropogenic influences, however, transportation of P to the aquatic environment has increased through mining and production of P fertilisers and their accumulation in cultivated, easily eroding surface soils, P-containing detergents, and municipal and industrial waste waters (Golterman 1973, Caraco 1993). Although P in soil particles may be more or less unavailable for plants, it may become available in the aquatic system (Hartikainen 1979). The most important mechanism for P release is reduction-induced release of Fe-bound P. In addition, during surface runoff, dilution of the thin film of soil water (with a higher ionic concentration) around the soil particle by water of low ionic strength may enhance desorption of P from particle surfaces.

1.4 Chemical fractionation as a tool for characterisation of sediment P

The question of the availability of soil P for plants encouraged soil chemists to study various chemical forms of P to determine the nutrient status of the soil and to study the chemistry and genesis of soils (Chang & Jackson 1957). The method initially developed was a sequential extraction or fractionation, in which soil P was separated into various binding and solubility fractions according to reactivity against different reagents. The principles of the fractionation methods are to displace PO_4-P from its sorption sites (through anion competition), to alter the adsorption surface, or to dissolve compounds containing P. The most easily desorbed and labile compounds are removed first with dilute reagents and the strength of the extractants increases stepwise, in order to separate more strongly bound P forms.

In the oldest methods, soil P was extracted with acids and bases to separate Ca-bound and apatite-P from P bound to Fe and Al oxides (e.g., Anderson Fisher & Thomas 1935, Williams 1937, Dean 1938, Ghani 1943, Williams 1950). On the basis of work by Turner and Rice (1954), Chang and Jackson (1957) developed a method which, unlike the earlier methods, was able to separate Al- and Fe-bound P using ammonium fluoride (NH_4F) and sodium hydroxide (NaOH), respectively. Other forms of P separated by this method were Ca-bound P extracted with sulphuric acid (H_2SO_4), reductant-soluble Fe-P separated by sodium dithionite ($Na_2S_2O_4$) treatment, occluded Al-P (and Fe-P) separated by repeating the previous extractions, and refractory P, which is mainly OP. The ammonium chloride (NH_4Cl) treatment in the beginning removed water soluble and loosely bound P as well as exchangeable Ca. This method and its modifications were widely used in soils and in lake sediments (e.g., Hartikainen 1979), but it was criticised because NH_4F, while extracting Al-P, was also found to dissolve Fe-P, overestimating Al-P at the expense of Fe-P (Bromfield 1967, Williams & al. 1971a). Another problem was transfer of Al- or Fe-bound P into Ca-bound forms in calcareous sediments (Williams & al. 1971b). Boström et al. (1982), Pettersson et al. (1988), and Carman and Jonsson (1991) summarise the development of P fractionation methods, compare different methods and discuss their shortcomings. Other method comparisons are presented, e.g., in Van Eck (1982), Barbanti et al. (1994), and Ruban et al. (1999).

Since the recognition of eutrophication of surface waters as an environmental problem, fractionation methods have been increasingly applied to investigate sinks and sources of P in lake sediments (Frink 1969, Williams & al. 1971a, b, Williams & al. 1976, Hartikainen 1979, Hieltjes & Lijklema 1980, Psenner & al. 1984) and in marine sediments (Holm 1978, Morse & Cook 1978, Lucotte & d'Anglejan 1985, Balzer 1986, Ruttenberg 1990, 1992, Jensen & Thamdrup 1993). Forms of P similar to those found in soil have been detected and characterised in aquatic sediments. Loosely bound, loosely adsorbed, exchangeable or soluble pore water P was extracted with NH_4Cl (e.g., Psenner & al. 1988, Hieltjes & Lijklema 1980), ammonium acetate (NH_4OAc; Van Eck 1982), sodium chloride (NaCl; Jensen & Thamdrup 1993), or magnesium chloride ($MgCl_2$; Ruttenberg 1992). Fe- and Al-bound P (or non-apatite P) has been extracted with NaOH (e.g., Williams & al. 1976, Psenner & al. 1984, Jensen & Thamdrup 1993) and Ca-bound and apatite P with HCl (e.g., Williams & al. 1971b, 1976, Hieltjes & Lijklema 1980, Psenner & al. 1984). Golterman (1996) replaced the relatively strong alkali and acid extractions with chelating agents (Ca-EDTA dithionite for Fe-P and Na_2-EDTA for Ca-P) to avoid hydrolysation of the most sensitive OP compounds during extraction. In aquatic sediments, P released in reducing conditions was considered an important P form, and different reducing agents were incorporated into the fractionation schemes. Chang and Jackson (1957) already had a step for separation of reductant-soluble Fe-P with dithionite ($Na_2S_2O_4$) in their procedure, and the same reagent (with or without chelating citrate) was used for lake sediments, although combined with bicarbonate buffer to avoid changes in pH (Mehra & Jackson 1960, Williams & al. 1980,

Psenner & al. 1984, Ruttenberg 1992, Jensen & Thamdrup 1993). In addition to dithionite, for example, hydrogen sulphide (H_2S, Carman & Jonsson 1991) and ascorbic acid (Anschutz & al. 1998) have been used for reduction of Fe in sediments. Ruttenberg (1990, 1992) made a major improvement by introducing a sodium acetate-extraction to separate authigenic apatite (carbonate fluorapatite, biogenic hydroxyapatite, and calcium carbonate, $CaCO_3$-bound P), which acts as a sink for P, from detrital apatite of igneous or metamorphic origin.

Inorganic P forms were initially emphasised in fractionation methods, partly because of a lack of suitable analytical methods for OP forms. Soil and sediment OP was traditionally extracted with alkali-solution (e.g. NaOH) or with acids and simply determined as the difference between total P (TP) and inorganic P (Mehta & al. 1954, Legg & Black 1955). Later on, Sommers et al. (1972) combined anion exchange chromatography with extractions, Bowman and Cole (1978) classified soil OP as labile, moderately labile, moderately resistant, and highly resistant, and Hedley & al. (1982) distinguished between OP forms of different binding strengths, including OP from lysed microbial cells. The well-known problem in extraction of OP was hydrolysation of easily-hydrolysable OP molecules into PO_4-P, either during extraction or during determination of PO_4-P with the acidic reagents of the molybdate blue method (Koroleff 1983). Attempts were made to minimise hydrolysis by dilution of NaOH, or using chelating agents, e.g., nitrilo triacetic acid (NTA; Golterman 1982). In the method by Psenner & al. (1988) OP was separated into alkali-extractable OP and residual P, which is supposed to consist mainly of refractory OP. Later on, analytical methods improved and ^{31}P-NMR was used for identification of different groups of OP compounds. For example, ortho-P mono- and diesters, polyphosphates, phosphonates, and pyrophosphate have been identified in, for example, NaOH- or EDTA-extracts of sediments and soils (Ingall & al. 1990, Hupfer & al. 1995, Turner & al. 2003, Carman & al. 2000, Ahlgren & al. 2005).

Sequential extraction methods are useful because of their ability to define groups of similarly behaving compounds occurring in relatively small concentrations and present in other than pure mineral phases in the sediment (Ruttenberg 1992). Despite the methods being rough, they can be used for characterising sediment P assessing the proportion of P which may, under certain environmental conditions, become available for production of new OM in the marine system, or may be buried with sediment and removed from the nutrient cycle. Sequential extractions are operationally-defined, i.e., the results depend on the procedure and reagents used. Therefore, comparisons of results of different sediment P studies can be difficult because of the variety of fractionation methods used. Furthermore, concerning aquatic sediments, especially hypoxic ones, sampling practices can significantly affect the P fractions, particularly soluble P and Fe-bound P. The oxidation of Fe^{2+} is relatively fast (Davison & Seed 1983, Millero & al. 1987) and ferro-iron in reduced sediment is easily oxidised by atmospheric O_2 to the ferric form, which binds dissolved P from pore water (Mortimer 1942, 1971, Krom & Berner 1980). This problem has been overcome by shielding the sediment from atmospheric O_2 with, e.g., argon (Ar) or N_2 in a glove bag (Krom & Berner 1980, Wiltshire 1991, Jensen & Thamdrup 1993).

1.4.1 Previous phosphorus fractionation studies in marine sediments in the BS region

Holm (1978) found that non-apatite P and OP were higher in oxidised than in reduced surface sediment on the western coast of the BP. He also recorded a decrease in reductant-soluble P during negative redox turnover, while alkali-extractable and apatite-P remained constant. Forsgren and Jansson (1993) reported that Ca-bound P was enriched in shallow areas of the estuary of the river Öre (Sweden, northern BS), while alkali-extractable P was enriched in the deep, fine-grained areas of the estuary. Distribution of residual P, in contrast, was relatively even. In the Pomeranian Bay, Ca-bound P was more abundant than Fe- and Al-bound P, occluded P was occasionally high in the upper reaches of the estuary, and OP was high in OM-rich sediments (Frankowski & al. 2002). OP also dominated in the surface sediments in the AS, where detrital apatite-P was the second most abundant P form, followed by redox-sensitive P and authigenic apatite-P (Virtasalo & al. 2005). In the GR, inorganic P was higher than OP, and redox-sensitive P dominated in the surface sediments (Aigars 2001). Redox-dependent P also dominated in the surfaces of mud sediments in the Kiel Bight (Balzer 1986). According to Carman and Jonsson (1991), redox-sensitive P was high in the near-shore sediments and in the archipelago in the western BP, although apatite-P dominated in most sediments in that sea area. Lehtoranta (1998) suggested that residual P as well as Fe- and Al-bound P dominated in the surface sediments in the eastern GoF. In the southwestern BS (Aarhus Bay, Kattegat, and Skagerrak; Jensen & Thamdrup 1993, Jensen & al. 1995), Fe-bound P and apatite-P were the most abundant P forms, followed by refractory OP. P forms extracted in marine and estuarine sediments in the BS region have often been relatively similar. However, all of these studies have used different fractionation procedures, thus, the separated P fractions are not completely comparable. This demonstrates the need to examine the chemical composition of sediment P in different areas of the BS using the same method.

2. OBJECTIVES OF THE RESEARCH

The main objective of this work was to investigate and compare the vertical distribution of sediment P and its chemical character in differing environments in the GoF and AS, northeastern BS (**III–V**). The purpose was to estimate how much of the P in bottom sediments is removed from the nutrient cycle, and how much of the sediment P reserves are in forms that can be released from the sediment to the overlying water with time, thus potentially contributing to eutrophication. The environments explored were two shallow estuaries (**III**), poorly oxygenated open sea sediments with varying concentrations of OM (**IV**), and shallow coastal sediments overlain by oxic near-bottom water (**V**) in the northeastern BS. The same methods were used in the differing environments to get comparable results. Furthermore, the occurrence and distribution of different P forms were examined to determine how they were related to chemical and physical characteristics of the sediments and to the chemistry of the sediment pore water and near-bottom water to get a more comprehensive insight into the chemistry of P and its behaviour at the sediment-water interface.

The principal method used was the sequential extraction of sediment P. In several studies using P fractionation methods, the theoretical basis for the separation of different P forms and the working practices in the laboratory are not described in detail, which often makes the methods difficult to apply. Thus, an attempt was made to evaluate the validity of the method against the theory behind it by analysing the elements extracted along with P, to assess the reproducibility of the method, and to describe the working practices in detail (**I**). In addition, the suitability of the chosen fractionation method for sediments in the study area, and the sampling and sample storing practices, were assessed to ensure reliability of the results (**II**). Furthermore, additional studies were made to assess the changes occurring in sediment P when sampling was performed in spring veresus autumn, and to investigate variations in the vertical distribution of P within one sedimentation basin.

3. MATERIALS AND METHODS

3.1 Application and evaluation of the P fractionation method and working practices (I, II)

The method used for sediment P fractionation was the five-step procedure presented by Jensen and Thamdrup (1993), which separates six sedimentary P forms: 1) loosely adsorbed and pore water P (extracted by NaCl); 2) redox-sensitive P bound to hydrated oxides of reducible metals, mainly Fe ($Na_2S_2O_4$, in bicarbonate buffer, $NaHCO_3$, at pH 7); 3) labile OP (non-reactive P in NaOH, calculated as the difference between TP and PO_4-P); 4) P bound to oxides of metals not reduced in the previous step, e.g. Al (PO_4-P in NaOH); 5) Ca-bound P, mainly from apatite minerals (HCl); and 6) residual P, mainly refractory OP (HCl). These six fractions are referred to later as NaCl-iP, NaBD-iP, NRP, NaOH-iP, HCl-iP, and Res-P, respectively.

The suitability of a P fractionation method for characterisation of P forms depends on the environment, the material to be studied, and on the type of material for which the method was originally designed. For instance, a high abundance of clayey material, OM, and calcareous minerals may affect the ability of extraction procedures to distinguish between different P forms (Ruttenberg 1992). The sediments in the study area are typically poor in $CaCO_3$, but high in OM and Fe (Winterhalter & al. 1981, Emelyanov 1988, Conley & al. 1997). Thus, it was anticipated that Fe-bound and OP forms would be of major importance. The extraction scheme developed by Psenner et al. (1984) and Psenner et al. (1988) for lake sediments and modified by Jensen and Thamdrup (1993) for marine sediments was chosen because it emphasises Fe-bound P that is sensitive to redox-changes, typical for the sediments in our study area. It also divides OP into two fractions, labile and refractory OP. This method has been criticised for overestimating Fe-bound P at the expense of Ca-bound P in carbonate sediments (Jensen & al. 1998). However, that was not considered a critical factor because of the low content of $CaCO_3$ in the study areas.

In many P fractionation studies the sediment sample has been dried prior to extraction (e.g. Ruttenberg 1992, Filippelli & Delaney 1996). However, only a few studies have assessed the effects of sediment drying on P fractions, especially in hypoxic sediments. Exposure to air readily oxidises reduced Fe-compounds that, consequently, bind PO_4-P (Krom & Berner 1980, Wiltshire 1991). Furthermore, drying and freezing may result in partial degradation of OP compounds and thus increase dissolved and Fe-bound forms of P (Jensen & Thamdrup 1993, Jensen & al. 1995, Goedkoop & Pettersson 2000, Lukkari, unpublished data). To diminish changes caused by pre-treatment of the sediment, Psenner et al. (1984), Psenner et al. (1988), and Jensen and Thamdrup (1993) fractionated fresh sediment, and the latter authors performed extraction of the two most sensitive P forms under N_2 atmosphere (atm).

3.1.1 Evaluation of the P fractionation method (I)

3.1.1.1 Modification of the method

Jensen and Thamdrup (1993) modified the method by Psenner and co-workers (1988) in an attempt to minimise replacement of Ca (Hieltjes & Lijklema 1980, Pettersson & al. 1988) in the first step by replacing NH_4Cl with NaCl. Furthermore, they added rinsing steps after steps I–IV to minimise tailing, i.e., the transfer of P left in pore water to the following fraction. They also used more dilute NaOH to diminish hydrolysation of easily hydrolysable OP compounds (Hupfer & al. 1995), which would overestimate the PO_4-P in NaOH, i.e., Al-bound P.

In this work, the procedure by Jensen and Thamdrup (1993) was modified slightly further (**I**). The last step separating refractory OP was replaced by the corresponding step in the SEDEX-method (Aspila & al. 1976, Ruttenberg 1992), because this step has been shown to produce accurate results (Ruban & al. 1999), and it seemed easier to carry out. In addition, a smaller sediment-to-solution ratio was used to ensure that the extractants would not be saturated with respect to P in P-rich sediments, and that there would be enough extraction solution for all determinations. Furthermore, NaOH-extractable OP (NRP) was treated in a different way than described in Jensen and Thamdrup (1993) and in Paludan and Jensen (1995). The separation of labile and refractory OP was made on the basis of their dissolution (i.e., particle size). OP dissolved (<0.4 μm) in NaOH was considered labile OP (NRP), and particulate P (>0.4 μm) in NaOH was considered more recalcitrant and included in the refractory OP fraction (Res-P). The rationale for this modification was supported by e.g. the findings that in coastal seawater, microorganisms use primarily low-molecular-weight dissolved OM (Ogura 1975), and that larger molecules and particles are supposed to degrade more slowly than smaller ones and preferentially form complexes with, for example, Al^{3+} and Fe^{3+} (Hargrave 1972, Steinberg & Muenster 1985). The P fractionation procedure (**I**, Fig. 1), sample treatment, and analytical methods are described in detail in paper **I**.

3.1.1.2 Co-occurring elements in the extracts

Several studies describe testing sequential extraction methods using pure mineral phases that participate in P binding and other P containing compounds that mimic those occurring naturally (e.g., Ruttenberg 1992). In this study, however, the validity of the method was evaluated by analysing elements that were released in different extracts simultaneously with P, in order to determine whether there was any support for the theoretical basis of the method. The test sample was a commercial reference material, BCR-684 (calcareous sediment from the river Po, Italy). This reference material is certified for five forms of P separated by another fractionation scheme (Ruban & al. 1999, 2001, Williams & al. 1976). Nevertheless, it was used because it was homogeneous and known to contain detectable amounts of different forms of P. In addition, two dissimilar samples, oxic and reduced, were collected from the Fe- and OM-rich BS sediments, and their extraction results were compared to those obtained for the Ca-rich reference material (**II**).

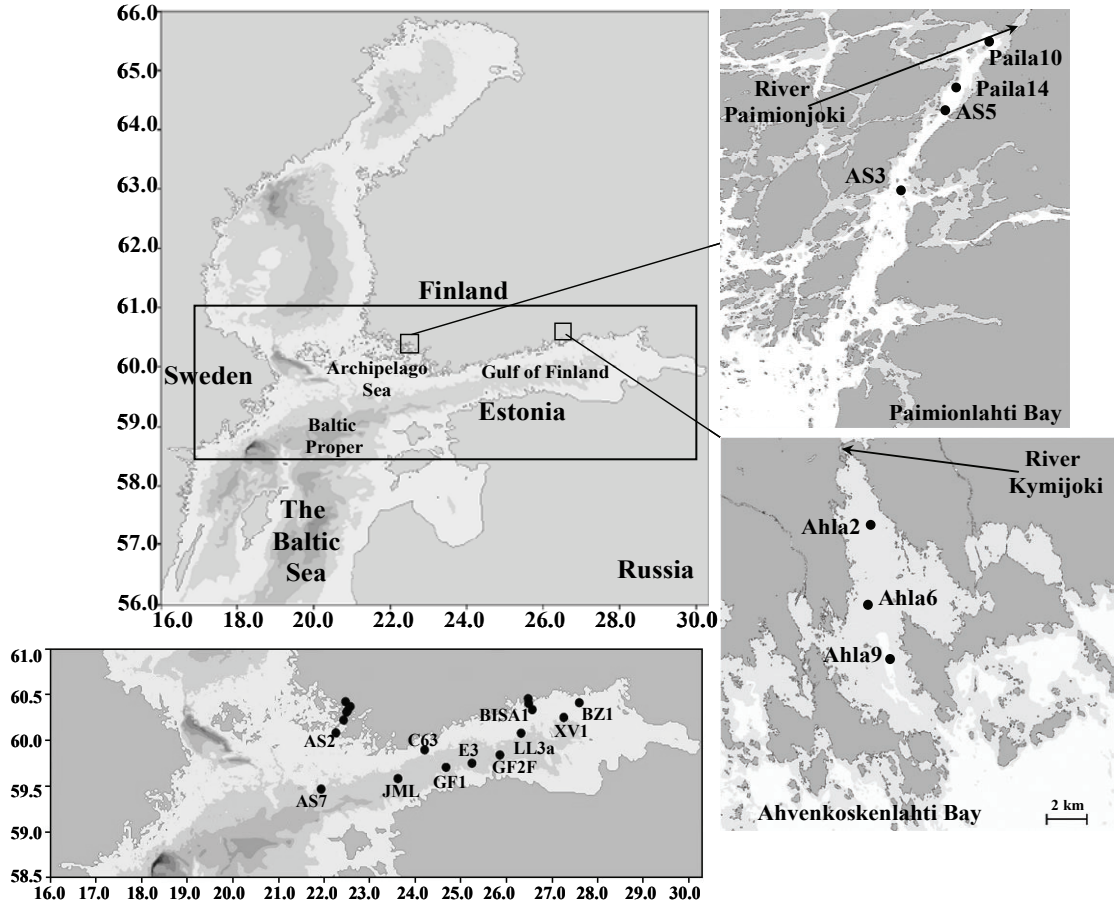
In addition to spectrophotometric P determination (dissolved inorganic P, DIP, and TP; Koroleff 1983), the extracts were analysed for total concentrations of dissolved (T_{diss}) Fe, Mn, Al, Ca, Mg, Si, and P by ICP-OES. In addition, concentrations of total P, as well as total Fe, Mn, Al, and Ca were determined in the reference material with ICP-AES after complete digestion. The analytical methods and sample treatments used in spectrophotometric analyses of PO_4-P and TP, in ICP-OES analyses of elements in extracts, as well as in sediment digestion and ICP-AES determinations, are described in paper **I**. Furthermore, when assessing the analytical reliability of the extraction method and working practices, the matrix effect was first tested to find any possible errors in PO_4-P and TP analysis that could be caused by the different extract matrices, i.e., solutions of different chemical composition used in the various steps.

3.1.1.3 Reproducibility of the fractionation method

Reproducibility of the method was assessed by comparing basic statistical parameters calculated from fractionation results of twenty replicates of the reference material. All samples were extracted in separate sets of samples to find out whether different extraction times (e.g., using extractants prepared at different times) would cause any deviation in the results. In addition to the reproducibility of the method in determining P in the six fractions (the spectrophotometric analysis of DIP and TP), the reproducibility of the method was assessed for other elements determined with ICP-OES. A good reproducibility of the procedure for other elements creates the basis for utilisation of the elemental composition when assessing the validity of the method.

3.1.2 Evaluation of the effects of sampling practices and sample storage on P fractions (II)

In order to ensure the reliability of the fractionation results for the chemical characterisation of P in oxic and reduced sediments, the sensitivity of the P fractionation method to sampling and sample storing practices was assessed (**II**). Shielding with N_2 is a common method to avoid changes caused by sample oxidation during sampling and sample storage.



Site	Latitude	Longitude	Site	Latitude	Longitude	Site	Latitude	Longitude	Site	Latitude	Longitude
Paila10	60°22.14′	22°34.81′	GF2B	59°50.31′	25°51.41′	AS7	59°28.00′	21°56.50′	BZ1	60°24.64′	27°36.32′
Paila14	60°19.50′	22°31.35′	GF2K	59°50.47′	25°52.31′	JML	59°34.91′	23°37.60′	BISA1	60°20.12′	26°34.55′
AS5	60°18.47′	22°30.03′	C63	59°53.72′	24°12.70′	E3	59°44.95′	25°15.06′	Ahla2	60°27.31′	26°28.98′
AS3	60°13.27′	22°25.98′	LL3a	60°04.67′	26°19.73′	GF1	59°42.31′	24°40.92′	Ahla6	60°25.30′	26°28.60′
AS2	60°04.88′	22°15.88′	XV1	60°14.94′	27°15.90′	GF2F	59°50.38′	25°51.86′	Ahla9	60°24.12′	26°29.73′

Fig. 2. Locations of the sampling sites in the northeastern BS.

However, there are very few studies describing the effects of the shielding (Wiltshire 1991). In addition, to prevent changes in the sample, the analyses should be carried out as soon as possible after sampling. This, however, is not always possible with marine sediments, and sample storage is necessary. Therefore, it is important to know how P fractions in fresh sediments change during storage and whether those changes can be diminished by shielding with N_2.

3.1.2.1 Oxygen-induced changes in P fractions

Oxygen-induced changes in P fractions were studied with oxic and reduced sediments. The brown, oxic, surface sediment was collected from site AS5 (water depth 33 m) in Paimionlahti Bay, (in August 2003; see below, Fig. 2). The reduced, dark grey sediment sample was taken from the hypoxic site GF2B (in April 2004) located in a sedimentation basin in the central GoF (water depth 85 m). The sediment samples were taken with a Gemax gravity corer and sectioned under N_2 atm. Homogenised samples of both oxic and reduced sediment were divided into two portions: one portion was always treated in N_2 atm (i.e., N_2 atm treatment) and the container was immediately sealed in a gas-tight plastic bag filled with N_2. The other portion was allowed to react with atmospheric O_2 (normal atm treatment) for 0.5 h before sealing the container. For both treatments, the reduced sediment (GF2B) samples were fractionated four times and for both treatments, the oxic sediment (AS5) samples were fractionated six times at different time intervals. Three (or two) replicates of each treatment were extracted according to the procedure presented in paper **I**. However, in steps I–II the sediment samples kept in N_2 atm were extracted under N_2 atm in a glove box, while the samples exposed to O_2 and stored without N_2 shielding were extracted under normal atm. Details of the sampling and sample treatment are presented in paper **II** and analytical methods in paper **I**.

3.1.2.2 Preservation of P fractionation extracts

Storage-induced changes in DIP and TP in extracts were assessed to determine how rapidly the measurements should be made after completing each extraction step in order to get reliable results. This experiment was done by analysing extracts stored for different periods of time, either unpreserved or preserved with acid. The details of this test are presented in paper **II** and analytical methods in paper **I**.

3.1.3 Assessment of change in forms of surface sediment P from spring to autumn

The sampling cruises were done at the end of August (in 2003 and 2004) and at the end of April (in 2004). To assess whether this seasonal difference affected the chemical composition of sediment P, a comparison was made between samples collected in April and in August 2004 at two sampling sites, GF2F and LL3a. Site GF2F is located in the poorly oxygenated basin in the central GoF (Fig. 2) and it was hypoxic in April and in August. Site LL3a, a shallower site located eastwards from GF2F, was slightly oxic in April and better oxygenated in August. In April, both sites were sampled down to a depth of 25 cm, while in August, samples were collected only from the topmost 5-cm layer (in 1-cm sections) because it was assumed that most of the changes would occur in the surface layer. The samples were protected from atmospheric O_2 during sampling, storing, and during the first two steps of extraction. Analytical methods for determining P fractions are described in paper **I**.

3.1.4 Assessment of variation in P forms and in their vertical distribution within one sedimentation basin

Sedimentation may vary considerably within relatively small areas in the AS and in the GoF mainly because of the variable bottom topography (Winterhalter & al. 1981, Vallius 1999a, Virtasalo & al. 2005). The shallow areas, where wave action reaches the bottom water (and seabed), are especially susceptible to resuspension and transportation of fine-particulate surface sediment. However, resuspension and transportation may also occur in deep areas, for instance, as a result of local water currents near the bottom (Vallius 1999a). Because of the variation in sedimentation, the distribution of sediment P may also vary within a relatively small area. This phenomenon was investigated by comparing the vertical distribution of different forms of P among three sampling sites (GF2F, GF2K, and GF2B; Fig. 2) located within the GF2 basin in the central GoF.

3.2 Study area

3.2.1 General description of the study area

All study sites were located in the northeastern BS (Fig. 2). The two shallow estuaries, Paimionlahti Bay (Paila Bay) and Ahvenkoskenlahti Bay (Ahla Bay) are located in the AS and in the eastern GoF, respectively (**III**). The poorly oxygenated open sea sites extend from the northern BP to the eastern GoF (**IV**) and the shallow coastal sites were located in the AS and on the northern coast of the GoF (**V**). Locations of the sampling sites are presented in Fig. 2.

The GoF is a shallow non-tidal bay, which, through its bottom topography, forms a straight extension to the BP. Its surface area is ca. 29 600 km^2 and the mean depth is 37 m (the deepest basin is 123 m). Salinity is low (5–10 PSU), and intrusions of (often poorly oxygenated) bottom water from the BP creates salinity stratification in the GoF. The halocline varies from around 60 to 80 m in depth in the western and central GoF, while the shallow, low-salinity eastern end has no halocline (Kullenberg 1981, Alenius & al. 1998). The northern coast of the GoF is indented and has numerous small islands. The bottom topography is also variable, consisting of different bottom types: rocky areas alternate with numerous small sub-basins, and the deeper parts are filled with soft sediments (Winterhalter & al. 1981). Several small rivers discharge into the GoF, and the River Neva, the largest river in the BS, discharges into the eastern end of the Gulf.

The AS (surface area 8300 km^2) is located southwest of the Finnish coast in the area where the GoF, the Bothnian Sea and the northern BP meet. Its shoreline is indented and the whole sea area is characterised by thousands of small isles and variable bottom topography that restricts exchange of water. The mean depth of the AS is only 23 m, although the deepest basins are more than 100 m deep, and the salinity varies from about 4 to 7 PSU (Virtasalo & al. 2005, Winterhalter & al. 1981). Although lacking salinity stratification, like the shallow basins on the northern coast of the GoF the water column is often thermally stratified seasonally (Virtasalo & al. 2005, Kotilainen & al. 2007). The basement in the study area in the AS as well as in the northern GoF consists of Paleoproterozoic crystalline bedrock (Koistinen & al. 2001) usually covered by till, unless it is exposed because of erosion. Late glacial and postglacial clays, silt, and sand often cover the bedrock and till. Modern sediments in the study area are mainly muddy clays rich in Fe and OM but poor in $CaCO_3$ (Winterhalter & al. 1981, Emelyanov 1988, Conley & al. 1997).

3.2.2 Environmental properties at the sampling sites

Sampling sites Paila10, Paila14, AS5, and AS3 (Fig. 2) were located in Paila Bay (surface area 144.7 km^2), on the southwest coast of Finland, and form a transect along the estuary of the River Paimionjoki (drainage area 1088 km^2) (HELCOM 1998, Kangas & al. 2003). Site Paila10 was the innermost and shallowest site in the estuary, AS5 was the deepest, and AS3 was the outermost site. During sampling, the concentration of dissolved O_2 in the near-bottom water was 1.7 ml l^{-1} at AS5, while it was >2 ml l^{-1} (i.e., oxic) for the rest of the sites in Paila Bay (Table 1). Salinity was around 6 PSU at all sites in Paila Bay. Sites Ahla2, Ahla6, and Ahla9 were located in Ahla Bay (surface area 52.5 km^2) near the western branch of the River Kymijoki (drainage area 37 159 km^2 of the whole River Kymijoki), on the northeastern coast of the GoF (HELCOM 1998, Kangas & al. 2003). Ahla2 was the innermost and shallowest (4 m) site and Ahla9 was the outermost and deepest site (although only 13 m) in Ahla Bay. All sites in Ahla Bay were oxic during sampling and salinity in the Bay is about 5 PSU maximum (Kangas & al. 2003).

The Geological Survey of Finland (GTK) provided sediment descriptions for all the sites sampled for P fractionation. Sediments in both estuaries were mainly muddy clay covered by a brown, fluffy surface layer (1–2 cm). In Ahla Bay the brown surface layer was thinner than in Paila Bay. Below the surface, sediments usually had light and dark grey and black laminae (mostly in the upper part of the sediment cores), which were partly disturbed or bioturbated.

The shallow (water depth <60 m) coastal sampling sites AS2, C63, BISA1, and BZ1 were located in the AS and on the northern coast of the GoF (Fig. 2). The near-bottom water at all coastal sites was oxic and salinity ranged from 5.7 to 6.6 PSU (Table 1). At the shallow coastal sites the sediment was also mainly muddy clay. The two westernmost sites had a brown (ca. 1 cm) fluffy layer on top of the sediment. The easternmost site (BZ1) also had a very thin brown layer on the surface, while at the neighbouring site (BISA1) white bacterial growth covered the fluffy black sediment. At the other sites, the sediment was usually laminated with black and grey, partly disturbed layers, except at site C63 where the sub-surface sediment was homogeneous and very hard below ca. 15 cm depth.

Table 1. Water depth (m), salinity (PSU), and concentrations of dissolved O_2 (ml l^{-1}) and dissolved and total species (µmol l^{-1}) in the near-bottom water. Incubation-derived PO_4-P flux is presented in µmol m^{-2} d^{-1}.

	Depth	Salinity	O_2	PO_4-P	TP	NO_3-N	NH_4-N	TN	SiO_4-Si	Fe	Mn	PO_4-P flux
Paila10	12	-	6.2*	0.4	1.8	0.4	5.1	33.6	20.4	0.1	1.6	-
Paila14	29	6.2*	2.9	0.7	2.5	7.6	7.7	45.1	23.7	0.7	6.0	278
AS5	33	6.3*	1.7	0.9	3.2	14.1	7.2	41.4	27.7	1.4	10.2	-4.2
AS3	19	6.3*	6.1	0.3	3.2	1.5	2.3	44.1	14.3	0.4	1.1	24.4
Ahla2	4	-	6.4*	0.9	2.3	3.6	8.5	37.9	24.1	5.2	2.7	-
Ahla6	7	-	4.3*	1.6	2.9	3.1	8.6	47.8	19.3	1.5	0.9	-
Ahla9	13	-	4.5	2.9	4.0	3.6	10.8	34.7	21.7	3.0	0.9	671
AS2	47	6.6*	4.9	1.4	3.2	3.6	3.5	34.4	16.9	8.9	2.2	46
C63	45	6.0*	8.6*	1.0	1.9	3.3	0.6	27.7	15.8	0.5	0.4	-
BISA1	29	5.7*	3.8	2.8	6.5	5.4	8.0	43.2	26.2	1.1	5.2	1065
BZ1	40	6.1*	3.4	4.3	5.9	11.9	10.8	41.4	37.8	12.3	15.0	193
AS7	71	8.6*	1.6	3.4	2.8	5.5	5.8	28.7	48.7	0	2.2	198
JML	79	8.2*	1.8	3.9	4.0	3.6	2.5	19.7	44.9	0.5	4.3	-209
GF1	83	8.5*	0	5.2	7.6	0.4	6.6	32.0	53.8	0.2	12.2	1370
E3	89	9.7*	0.4	3.8	3.5	1.6	8.3	10.3	53.4	0.9	16.6	207
GF2B	85	9.5*	0.8	3.4	4.1	8.0	2.8	28.8	47.3	0.6	4.3	-135
GF2F	84	9.5*	0.8	3.3	3.4	6.9	2.5	27.5	48.7	0.5	2.4	357
GF2K	83	9.5*	1.0	4.1	4.8	7.4	3.3	31.2	50.8	0.8	13.0	299
LL3a	63	8.2*	2.4	3.1	3.7	10.4	0.8	29.7	40.1	0.8	1.6	-245
XV1	58	7.0*	2.5	2.8	5.6	11.6	5.1	43.7	43.5	1.2	13.9	1774

Values labeled with an asterisk (*) were determined ca. 1 m above the sediment.

Sampling sites in deep (water depth >60 m, 58 m at XV1) open sea areas formed a continuum beginning from the northern BP (AS7) and terminating at the eastern GoF (Fig. 2). The deepest site (E3; 89 m) was located in the central GoF (Table 1). The two easternmost sites, XV1 and LL3a, were slightly oxic, while the rest of the open sea sites were hypoxic (<2.0 ml l^{-1}). Salinity ranged from 7.0 to 9.7 PSU, being highest in the deepest basin. Sediments were mainly muddy clay. The surface sediment was fluffy and, occasionally, embedded with a brown lamina. Four sites (AS7, E3, GF2F, and XV1) had white bacteria growth on top of the sediment. Between the laminated (grey and black) units, the sediment was partly disturbed (bioturbated).

The three sites sampled for studying the variation in vertical distribution of sediment P forms within one sedimentation basin formed a transect (from southwest to northeast) across the GF2 basin in the central GoF. This basin was chosen because it is relatively deep (84 m, on average) and it has been considered a good area for studying sedimentation and composition of modern sediments (Vallius 1999b). The distance between site GF2B and site GF2K was about 0.5 nautical miles, and site GF2F was located between them (Vallius 1999b). These sites had quite similar sediments: white bacterial growth on top of the fluffy, clayey mud surface, which covered laminated (thin black, light grey and dark grey laminae) muddy clay. Below that, the sediment consisted of more homogeneous units.

3.3 Sampling and analytical methods (III, IV, V)

Methods used in sampling sediment, near-bottom water, and pore water, as well as analytical methods used for determination of their elemental composition and other chemical and physical properties are presented in detail in papers **III**, **IV**, and **V** and described only briefly here. All determinations are not available from all of the sampling sites, but for the most part, the same methods were used at all sites in the three differing environments, allowing comparison of the results.

3.3.1 Sediment

Sampling sites were selected based on information from echo sounding profiles. Usually, soft-bottom sediments from accumulation areas were selected. One of the sampling sites, however, represents a transportation area (C63). Sediment samples were collected on three cruises of the R/V Aranda: in August, 2003 (sites Paila10, Paila14, AS5, AS3, AS2, AS7, JML, and GF1), in April, 2004 (C63, E3, GF2F, GF2K, GF2B, LL3a), and in August, 2004 (Ahla2, Ahla6, Ahla9, BISA1, BZ1, and XV1, as well as surface sediment at LL3a and GF2F). The small vessels R/V Aurelia and R/V Muikku assisted in sampling at the shallowest sites in the estuaries.

The sediment samples were taken with a Gemax gravity corer. Two parallel cores from each site were sectioned under N_2 atm. The water column above the sediment was first sampled for determination of nutrients and dissolved Fe and Mn, and the core was cut into 1-cm slices, usually down to a depth of 25 cm. Corresponding depth layers of two parallel cores were pooled and stored (under N_2 atm) at 5°C (in the dark) until analysis. Another pair of sediment cores was sectioned at the same intervals (without N_2 atm) and the samples were immediately frozen (-18°C) and later freeze-dried and homogenised for total analysis of P (TP_{sed}), Fe, Mn, Al, and Ca. The sediment cores from sites GF2B, GF2F, and GF2K were sub-sampled for P fractionation so that the sample depths would represent approximately similar ages. The careful evaluation of the corresponding sedimentary units was based on sediment descriptions of split cores (A. Kotilainen, GTK, pers. com.).

One sediment core was used for determination of redox potential, pH, and temperature. Measurements were made with electrodes from the water ca. 5 cm above the sediment, and at 1-cm intervals from the sediment surface, down to ca. 10 cm depth. The redox potential is considered descriptive only (Stumm & Morgan 1996, Drever 2002) because these sediments were largely anoxic and because hydrogen sulphide (H_2S), present in some depth layers, is deleterious to electrodes.

One core from each site (except sites C63 and E3) was sectioned for sediment ^{137}Cs-dating. For most of the sites, ^{137}Cs activity was determined at the Finnish Radiation and Nuclear Safety Authority (according to Kyzyurov & al. 1994, Kankaanpää & al. 1997, Mattila & al. 2006) for calculation of sediment accumulation rate estimates (SAR values). Within the research area, ^{137}Cs peak values indicate sediment deposition in 1986 (the fallout following the Chernobyl accident). SAR values for sites in Paila Bay, AS2, AS7, JML, and GF1 are published in Mattila et al. (2006). For the rest of the sites, ^{137}Cs determinations and SAR estimates were made at GTK.

Particle size distribution was determined at GTK by sieving (particles Ø >60 µm) and with a Sedigraph analyser (Ø <60 µm). Total carbon (TC), total organic carbon (TOC), nitrogen (TN), and sulphur (TS) were determined with a LECO CNS-2000 analyser at Pirkanmaa Regional Environment Centre.

Phosphorus fractionation was done as described in paper **I**, except that fresh sediment (equivalent to 0.50 g dry matter, DM) was extracted, with two replicates. In addition, in extraction steps I–II, the sediment samples were treated under N_2 atm to avoid

oxidation. Details of the sample treatment under N_2 atm are presented in paper **II** and analytical methods in paper **I.** Jensen and Thamdrup (1993) divided the six P fractions into mobile and immobile P. The mobile P fraction includes NaCl-iP, NaBD-iP, and NRP, and the immobile P fraction includes NaOH-iP, HCl-iP, and Res-P (see also Rydin 2000). Several authors who have studied sediment P fractions in the marine environment use the term "reactive" P to describe P that is available to bacteria and algae or undergoes changes and diagenetic transformations in the sediment (i.e., degradation, sorption, desorption, dissolution, or precipitation; Froelich & al. 1982, Froelich 1988, Louchouarn & al. 1997, Delaney 1998, Anderson & al. 2001). That is why the term "reactive" was chosen instead of "mobile" P.

Sedimentation of P was calculated by multiplying the total concentration of extractable P (TP_{extr}), i.e., the sum of P in the separate fractions, in the sediment surface layer by the SAR value at each site. Burial fluxes for P were calculated by multiplying the immobile P (including the buried part of sediment reactive P; see results and discussion section) in the surface layer by the SAR value. The burial efficiency of P was expressed as the proportion of immobile P in the surface layer as percentage of the TP_{extr}. It should be noted that the burial efficiency in this work includes all buried P forms. Thus, it is not directly comparable with burial efficiencies of reactive P calculated, for example, on the basis of results of the SEDEX-method (Ruttenberg 1992). Furthermore, using the P concentrations determined in the topmost 1-cm layers in calculations causes error because the layer consists of sediment of different ages at different sites, usually much older than one year. However, it is the best estimate for P concentration at the sediment surface available from this data. The annual average for the long-term P efflux from the sediment reserves at each site was calculated by calculating the difference between the reactive P in the surface layer and in the layer deposited in 1986 (i.e., the layer with the ^{137}Cs maximum) and by dividing the difference by the age difference of the layers (see results and discussion section).

3.3.2 Pore water

Sediment pore water in the sediment-water interface was collected in an Ar atmosphere (atm) using a whole-core hydraulic squeezer (Bender & al. 1987, Mäkelä & Tuominen 2003) from all sites, excluding the innermost estuary sites Paila10, Ahla2, and Ahla6, and the site C63. The sampling interval was calculated on the basis of the porosity of the sediment, the volume of the collected pore water, and the radius of the cylinder of the sampling corer (Bender & al. 1987, Mäkelä & Tuominen 2003). Pore water was analysed on board for the dissolved nutrients PO_4-P, nitrate (NO_3-N), ammonium (NH_4-N), and silicate (SiO_4-Si) (in filtered samples) with an autoanalyser (Lachat QuickChem 8000) by methods described in Hansen and Koroleff (1999). A portion of each of the pore water samples was acidified and later analysed for total dissolved Fe and Mn by ICP-AES.

At seven sampling sites (not from estuary sites, AS2, AS7, JML, and GF1) pore water was separated from the deeper sediment profile by centrifuging 1-cm sections of sediment (4000 rpm, 30 min). Sediment sectioning, transfer into tubes and filtration of the supernatant were carried out under N_2 atm in a glove bag. A portion of each of the pore water samples was acidified and later analysed for total dissolved Fe and Mn by ICP-AES.

3.3.3 Near-bottom water

Water column salinity, temperature, and dissolved O_2 were determined with a CTD instrument. The dissolved (filtered sample) nutrients, PO_4-P, NO_3-N, NH_4-N, and SiO_4-Si, as well as total (unfiltered) P (TP) and N (TN), were determined onboard with an autoanalyser (Hansen & Koroleff 1999). Dissolved O_2 in the near-bottom water (ca. 5 cm above the sediment) was determined by Winkler titration (Grasshoff 1983). The near-bottom water was analysed for dissolved and total P and N species as above.

For determination of incubation-derived PO_4-P flux, four intact replicate sediment cores were incubated at *in situ* temperature. Incubation was carried out in the dark, and the water column was gently stirred during incubation. The PO_4-P concentration was determined in the beginning and after a 5-h incubation, and the PO_4-P flux calculated (per surface area) on the basis of the concentration difference.

3.4 Statistical analyses

When assessing the reproducibility of the fractionation method (**I**), basic statistical parameters (average values, standard deviation, and coefficient of variation) were used to describe the differences between twenty replicate samples. The statistical significance of differences in P fractions caused by long-term storage was tested using the t-test for paired samples. The differences between the two types of sediment sample treatment and storage were tested using the t-test for unpaired samples (allowing unequal variances). Differences of $p<0.05$ between average values were considered significant. Elemental composition was determined only from two replicate samples (as well as P factions at the end of the experiment), thus, only trends in changes could be studied (**II**).

In papers **III–V**, statistical analyses were carried out using the mixed model (run with the SAS program), to determine which variables (elements in sediments and extracts) explain the different concentrations of P in the different fractions. The mixed model was chosen because the observations were correlated. The sampling site was set as a random variable, and the sediment depth layer was treated as a repeated factor. The dependence was tested with the F-test (significant when ≤ 0.05). Parameters for the mixed model were chosen on the basis of their mutual relations. They were studied with the Pearson correlation, considering a probability of <0.0001 to be statistically significant, and with principal components analysis carried out on the basis of Spearman correlations.

Discriminant analysis (DA, stepwise) was run (with the SPSS program) to determine whether the chemical composition of sediment P would differ significantly at different sampling sites so that they would form separate groups. An a priori-assumption in the analysis was that the sampling sites located in estuaries, in shallow coastal areas (water depth <60 m; including site XV1), and in deep (>60 m) open sea areas will form separate groups with respect to different forms of P. Data for NRP and HCl-iP fractions were normally distributed but a logarithmic ($\log_{10}$) transformation was made for the NaCl-iP, NaBD-iP, and NaOH-iP fractions, and square root transformation was done for the Res-P fraction to run the analysis. The NaCl-iP fraction, representing soluble P, did not seem to contribute to discrimination of the groups (F-test as a criterion, removal of fraction if $p<0.01$) unlike the other, solid phase P fractions; thus, it was excluded from the analysis. The statistical significance of the discriminant functions was tested with Wilks' λ and Chi-square tests.

4. RESULTS AND DISCUSSION

4.1 Suitability and reliability of the methods for characterisation of sediment P in the northeastern BS (I, II)

4.1.1 Reproducibility and reliability of the extraction method (I, II)

Good reproducibility of the P fractionation method is important to ensure that all results are comparable. First, the spectrophotometric method used in determination of PO_4-P and TP in the extracts was checked. The analytical error attributable to the varying composition of extracts (i.e., matrix effect) was negligible after sample dilution, that is, there was no statistically significant difference from the control solutions. Thus, determination of PO_4-P and TP were not considered to cause error.

The results (**I**, Table 1) showed good reproducibility for the fractionation method used to separate the six P forms. The P concentrations in each fraction varied very little: CV% was <10%, except for NaOH-iP and NRP, for which it was <15% and <27%, respectively. The NRP fraction is the sum of NRP in steps I–III, which probably causes cumulative error. However, taking into account the robustness of sequential extraction methods in general (i.e., separating hundreds of different P compounds into few fractions), it can be concluded that the analytical accuracy and reproducibility of this fractionation scheme is satisfactory and fractionation results are comparable. The reproducibility test was made with dry sediment, which is more homogeneous than the fresh sediments routinely extracted. However, the variation in replicates was also fairly small in fresh sediment samples (Jensen & Thamdrup 1993, **III**, **IV**, **V**).

The reproducibility of the fractionation method was also relatively good for the other elements in extracts analysed with ICP-OES (**I**, Table 2). With a few exceptions, CV% exceeded 20% only if the concentration of the element was low (<2 μmol g^{-1} DW). The highest variation occurred in the alkali extracts. Additionally, the relatively good reproducibility of the method for the co-extracted elements suggests that these elements can be used to characterise the components they are derived from.

The reliability and validity of the P fractionation method was evaluated by comparing P fractions and elemental compositions of the extracts in three differing sediment types: oxic and reduced BS sediments rich in Fe and OM but poor in $CaCO_3$, and oxic calcareous river sediment (reference material BCR-684, sediment from River Po, Italy).

Sodium chloride extract. The neutral salt solution extracted more P (i.e., loosely adsorbed and pore water P; NaCl-iP) from the Ca-rich river sediment than from the BS sediments (**II**, Fig. 4), and also more than commonly extracted from lake and marine sediments (Van Eck 1982, Pettersson & al. 1988, Jensen & Thamdrup 1993, **III**, **IV**, **V**). This suggests that the river sediment had a lower P sorption capacity than the BS sediments. The result is reasonable, because the river sediment was dried (Ruban & al. 2001), which could cause degradation of easily degradable OP compounds, increasing the NaCl-iP fraction (Jensen & Thamdrup 1993, Jensen & al. 1995, Goedkoop & Pettersson 2000, Lukkari, unpublished data). It is likely that the alkaline earth metals Ca^{2+} and Mg^{2+}, the most abundant elements in the NaCl-extract, were in exchangeable forms. As anticipated, the Ca-rich river sediment was higher in exchangeable Ca^{2+} than the BS sediments (**I**, Table 2; **II**, Table 2, Table 3, first column). Al and (oxidised) Fe are not expected to dissolve in NaCl (e.g.,

I, Fig. 4), while part of the easily reducible Mn as well as Si were probably in dissolved form in the fresh BS sediments. Dissolved Si is relevant when assessing P binding, because it can compete with PO_4-P for sorption sites on oxide surfaces, especially at elevated pH (Hingston & al. 1967, Ryden & al. 1987, Koski-Vähälä & al. 2001).

Sodium dithionite extract. The results for the fraction representing Fe-bound P sensitive to redox-reactions were well in accordance with the theory of its origin. This fraction was predominant in the oxic BS and river sediments. In contrast, the abundance of this P form was relatively low in the reduced BS sediment (**II,** Fig 4). Furthermore, the NaBD-extract was high in Fe, especially in the oxic Fe-rich BS sediment (**I**, Table 2; **II**, Table 2, Table 3). The reductant extracted about half of the total amount of Mn (**I**, Fig. 4). Aluminum, in contrast, is not sensitive to reduction and, accordingly, its concentration in the NaBD-extract was very low in all sediments. This is in agreement with the conclusion of Psenner et al. (1984) that the NaBD reagent is able to distinguish between P bound to oxides of reducible and non-reducible metals. This is important when considering eutrophication because hydrated oxides of Al, like those of Fe (III), are effective in P binding. Aluminum, however, is not dissolved in reducing conditions like Fe and, thus, it also retains P bound to it in reduced sediment. However, it is possible that bicarbonate, used as a buffer (pH 7) in the reductant, releases a small part of the P bound to Al-oxides (Olsen & al. 1954, Kamprath & Watson 1980, **III**). As found by Hartikainen et al. (1996) in lake sediments, some Si was in Fe-bound form in the test sediments. This is in accordance with the similar binding mechanisms of phosphate and silicate anions (Hingston & al. 1967, Ryden & al. 1987). The NaBD-extracts from the non-calcareous BS sediments were low in Ca and Mg, whereas that from the calcareous river sediment was high in Ca (**I**, Table 2). It is possible that the river sediment was high in exchangeable Ca^{2+}, and the preceding neutral salt extraction was not able to replace all of it on particle surfaces, so that some Ca^{2+} was released in the subsequent step. On the other hand, part of the Ca in NaBD in the calcareous river sediment may have originated from the fraction representing Ca-bound and apatite-P. In fact, Jensen et al. (1998) concluded that the specificity of the NaBD extraction for Fe-bound P is worse in $CaCO_3$-rich sediments. Similarly, Pettersson et al. (1988) and Uhlmann et al. (1990) suggested that part of the NaBD-extractable P could originate in Ca-bound forms. However, the over-estimation of Fe-bound P was not considered important in the non-calcareous sediments of the northeastern BS.

Sodium hydroxide extract. Most of the P in the alkali extraction (step III) is organic and in dissolved form. Thus, alkali-extractable OP forms the major portion of labile OP, i.e., the NRP fraction (**I–V**). ^{31}P-NMR determinations have shown that NaOH-extracts of sediments include pyrophosphate, polyphosphate, and orthophosphate monoesters and diesters (Hupfer & al. 1995, Ahlgren & al. 2005, Reitzel & al. 2006). The labile OP fraction (as well as refractory OP) was highest in the reduced BS sample collected from the deep basin in the open sea area (**II**, Fig. 4). This was reasonable because OM and OP accumulate in calm sedimentary environments (**IV**, **V**). Alkali can hydrolyse some of the easily hydrolysable OP into PO_4-P (Golterman 1996), for example, orthophosphate esters or polyphosphate into PO_4-P or pyrophosphate (Hupfer & al. 1995, Ahlgren 2006). However, the main part of NaOH-extractable inorganic P (NaOH-iP) represents P strongly bound to hydrated oxides of Al (Psenner & al. 1984, Jensen & Thamdrup 1993) and possibly to oxides of Fe not reduced in the previous step. Phosphorus and Al in this fraction were highest in the oxic BS sediment, collected from a shallow river estuary (**II**, Fig. 4; **I**, Table 2; **II**, Table 2, Table 3). This can be explained by the fact that the material transported from clayey soils by the river is rich in Fe and Al oxides that are able to retain P (Hartikainen 1979, Uusitalo 2004, Peltovuori 2006, **III**). The role of Al in P binding can be important in some lake environments (Hartikainen 1979, Kopáček & al. 2005), but its importance has been questioned in marine sediments, including in the BS (Forsgren & Jansson 1993). However, because the Al concentration is fairly high in the northern and northeastern BS (Leivuori 1998), separation of Al-bound P from redox-dependent Fe-bound P was considered a benefit of this fractionation method in this study area.

The main mechanism of P release through ligand exchange is the replacement of the PO_4-P group from the oxide surface with OH^- groups (Hingston & al. 1967), not dissolution of the compound providing sorption sites. In fact, part of the released Al probably originated from edges of partially disrupted mineral lattices and oxides, via formation of aluminate anions at highly elevated pH (Lindsay 1979, Barnhisel & Bertsch 1982). Furthermore, some P and Al dissolved in alkali can originate from organometallic complexes (Schnitzer 1969, Gerke & Hermann 1992, Lopez 2004). Humic acids form stable complexes with trivalent Al and Fe cations, which bind P (Schnitzer 1969). Williams et al. (1971c) and Paludan and Jensen (1995) reported that sediment contains OP associated with Al. In fractionation analysis, if the reduction of Fe is not complete, part of the Fe in disrupted oxides may be recovered in the subsequent alkali extraction step. However, considerably less Fe than Al was dissolved in NaOH (**I**, Fig. 4, Table 2; **II**, Table 2, Table 3). Thus, it is not likely that a significant part of the P in the NaOH-iP fraction was bound to Fe instead of Al. Excluding the final step, Si was most

abundant in the alkali extract (**I**, Table 2, Fig. 4; **II**, Table 2, Table 3). It is likely that a substantial part of it was of biogenic origin. Having a similar binding mechanism to PO_4-P, part of the Si in the NaOH-extract can be taken to represent silicate anions bound to Al-oxides (Hingston & al. 1967, Ryden & al. 1987, Hartikainen & al. 1996). In addition, NaOH can release some Si from silicate structures (Jones & Dreher 1996).

Hydrochloric acid extract. Ca-bound, mainly apatite-P formed a considerable proportion of the P in the test samples, especially in the reduced BS sediment and in the calcareous river sediment (**II**, Fig. 4). The HCl fraction probably also includes other Ca-containing minerals and some other inorganic P phases (Ruttenberg 1992). As expected, in the calcareous river sediment a major proportion of Ca was extracted in this step (**I**, Table 2, Fig. 4). Furthermore, the acid-extractable Ca (and Ca:P ratio in HCl) in the calcareous river sediment being higher than in the non-calcareous BS sediments was in agreement with the dissimilar natures of the test samples. The high Ca:P ratio in the river sediment signifies an abundance of carbonates, and a notably high concentration of acid-extractable Mg suggests the presence of dolomite. Pettersson et al. (1988) and Jensen et al. (1998) suggested that in calcareous sediments NaBD extraction would cause dissolution of some Ca-bound P, thus erroneously diminishing the HCl-iP fraction. In the present study, this side-reaction was found to take place in the calcareous river sediment (**I**, Table 2, Fig. 4). Another problem related to this fraction in calcareous sediments is that NaOH extraction prior to HCl overestimates HCl-iP, because dissolved Ca may transfer Al-bound P (and possibly Fe-bound P, depending on the procedure) to the apatitic fraction (De Groot & Golterman 1990, Benzing & Richardson 2005). However, this reaction pattern seems not to be a problem in non-calcareous BS sediments; NaOH-extractable Ca was almost undetectable (and NaBD-extractable Ca fairly low). The abundance of Fe, Al, and Si in the HCl-extract, especially in the BS sediments (**II**, Table 2, Table 3) suggests that some mineral structures were disrupted. One of the major shortcomings of the fractionation method used in this study is that it is not able to discriminate between detrital and authigenic apatite-P. This separation is important in many marine sediments because the authigenic apatite-P acts as a sink for P, while the detrital P is a relatively inert form of P (Ruttenberg 1992). Formation of authigenic apatite-P has been found to be related to active coastal upwelling, but Ruttenberg and Berner (1993) reported formation of authigenic apatite-P also in shallow OM-rich sediments. Thus, it is possible that this P form acts as a sink for P in BS sediments as well. In fact, Virtasalo et al. (2005) reported that about 10% of TP in the surface sediments in the AS was authigenic apatite-P. In the method used in the present study, the HCl-iP fraction represents both detrital and authigenic apatite-P and treats them both as immobile, buried P forms (Jensen & Thamdrup 1993). However, because the main objective in this study was to separate all the buried sediment P forms from reactive P forms that may be released from sediment over time, combining both apatite-P forms was not considered a problem.

Hydrochloric acid extract after combustion. The Res-P fraction represents refractory OP (Saunders & Williams 1955, Aspila & al. 1976, Psenner & al. 1988, Jensen & Thamdrup 1993) although this fraction also contains some inorganic P (Williams & al. 1967, Williams & al. 1980, Ruttenberg 1992, Lopez 2004). It can, for example, contain P occluded in oxide structures (Chang & Jackson 1957, Psenner & al. 1984) or contain some inorganic P from apatite or other minerals (Rutterberg 1992). As with the labile OP, refractory OP was highest in the reduced BS sediment collected from the deep open sea basin (**II**, Fig. 4). Generally, the total amount of OP, calculated as the sum of NRP and Res-P fractions, was higher in the OM-rich BS sediments than in the calcareous river sediment. The considerably high concentrations of Al, Si, Mg, and Fe in the acid extract following sediment combustion (**I**, Table 2, Fig. 4) indicate that the disruption of lattice minerals in this step was more drastic than in the preceding step separating Ca-bound and apatite-P. On the other hand, the extraction of Ca from the calcareous sediment was almost complete in the first acid-extraction, and there was very little Ca left in the residual fraction (**I**, Table 2, Fig. 4).

The comparison of P fractions and elemental composition of the extracts in the different sediment types indicated that the fractionation method gives reliable results for assessing six different sediment P forms in the northeastern BS. The sum of P in all steps (i.e., total extractable P, TP_{extr}) was lower than TP analysed after total digestion of the sediment (TP_{sed}), suggesting that some P was lost during the stepwise extraction. However, P determined from the sediment residue after completing the fractionation was negligible (**I**). Furthermore, the procedure extracted, on average, 95% of TP_{sed} in all sediment samples in the study area (**III**, **IV**, **V**). Generally, the percentage was highest in the areas high in TC and OP (i.e., NRP and Res-P fractions). This recovery is relatively good for a sequential extraction method, and the applied scheme can be considered to remove P efficiently.

4.1.2 Oxygen-induced changes in P fractions (II)

The sediment P fractions were investigated in the presence or absence of atmospheric O_2 during sampling and sample storage to determine which types of changes would occur, whether they could be

diminished by N_2 shielding, and to find out how long the samples could be stored and still provide reliable results.

Reduced sediment. The storage-induced changes in the P fractions were clearly more pronounced when the reduced sample was initially subjected to atmospheric O_2 than when it was shielded with N_2 (**II**, Fig. 2). The most marked changes had occurred by about 6 weeks of storage. The oxidation of Fe is relatively fast (Davison & Seed 1983, Millero & al. 1987). In fact, changes caused by O_2 were seen immediately: the loosely adsorbed and pore water P (NaCl-iP) remained in dissolved form in the sample shielded with N_2, while in the sample affected by O_2 it was retained by oxidised Fe-compounds and transferred to the subsequent fraction. The $T_{diss}Fe$ concentration in the NaBD-extract, being five times higher in the sample subjected to O_2 than in the N_2 shielded one, supports this conclusion (**II,** Table 2). Wiltshire (1991) reported a similar response of soluble P in sediment to O_2. In this study, Si, which competes with P for sorption sites, also stayed longer in dissolved form if the sample was protected from O_2. Generally, NaOH-extractable Fe seemed to be less affected by oxidation than reductant-soluble Fe in the reduced sediment sample. This indicates that Fe released by NaOH was not in a redox-sensitive form.

Of the other P forms, labile OP (NRP) increased during storage, the increase being slightly greater in the presence of O_2 (**II**, Fig. 2). NRP includes polyphosphates (Reitzel & al. 2006), which are storage compounds of microorganisms (Hupfer & al. 1995) preferentially synthesised in oxic conditions (Gächter & al. 1988, Uhlmann & al. 1990). However, some P seemed to be released from the refractory OP fraction (Res-P) over the course of several weeks in both oxic and anoxic conditions, which suggests that microbial degradation took place in both conditions.

Although Ca-bound and apatite-P is supposed to be a relatively stable P form in the sediment, especially detrital apatite, during long-term storage HCl-iP diminished if the reduced sample had the opportunity to react with atmospheric O_2 (**II**, Table 2). One explanation for this decrease is oxidation of pyrite (FeS_2, the presence of which was evidenced by the dark grey colour of the reduced sediment; Berner 1970) and consequent formation of sulphuric acid. Formation of the acid could result in dissolution of Ca-P on particle surfaces. This conclusion was supported by the concomitant decrease of $T_{diss}Ca$ in the HCl-extract and increase in the dissolved and exchangeable Ca (i.e., in the NaCl-extract) in the O_2-affected sample (**II**, Table 2). Furthermore, oxidation of FeS_2 produced Fe^{3+}, which partly increased $T_{diss}Fe$ (and P) in the reductant-soluble (NaBD) fraction (**II**, Table 2). Oxidation of pyrite in natural conditions when reduced sediment turns oxic can lead to a similar dissolution of Ca-bound and apatite-P. However, this reaction pattern would probably not release P to the overlying water because, at the same time, Fe-compounds oxidise and bind released P.

Oxic sediment. The findings made with reduced sediment were in agreement with those made with the initially oxic sediment. However, the O_2-induced changes were clearer in the oxic than in the reduced sediment. When the oxic sediment was not protected from atmospheric O_2, pore-water and loosely adsorbed P (NaCl-iP) was more effectively bound to the sediment. On the other hand, shielding the oxic sediment with N_2 had relatively little effect on the Fe-bound P (NaBD-iP) over 26 days of storage (**II**, Fig. 3). These results suggest that oxic sediments can be stored in N_2 atm for more than three weeks without any major decrease in Fe-bound P. There was probably enough O_2 in the sediment relative to the amount of reactive OM to prevent reduction of Fe. This conclusion was supported by the results for reductant-extractable Fe, which remained relatively high during the first weeks (**II**, Table 2). Apparently, also in oxic sediment, Fe-bound and dissolved P forms will change less if the sample is shielded with N_2 than if it is allowed to react with atmospheric O_2. However, reductant-soluble P (and Fe) diminished later in the N_2 shielded sample as well, indicating that the sample was slowly being reduced, probably due to microbiological O_2 consumption. In the O_2 affected sample, in turn, Fe-bound P increased over time (**II**, Fig. 3). Silicate reacted as expected: reductant-soluble Si was higher in the sample affected by O_2 due to enhanced retention on Fe oxides (**II**, Table 3).

In the oxic sediment, Ca gradually increased in the NaCl-extract and decreased in the HCl extract, especially if the sample was subjected to O_2. This response provides evidence of chemically- (and perhaps partly microbially-) induced dissolution of Ca minerals (**II**, Table 3). However, in the initially oxic sample, the changes were less clear than in the initially reduced one, which was probably higher in ferrosulphides (**II**, Table 2). Oxygen seemed not to affect markedly the alkali-extractable elements in the oxic sediment. However, as in the reduced sediment, without N_2-shielding the labile OP fraction (NRP) was slightly higher and increased more with prolonged storage than with N_2-shielding. In the oxic sediment, refractory OP (Res-P) remained higher in the presence of O_2 than when shielded with N_2. The differences were small, but binding of OP on oxide surfaces is known to retard degradation of OP in oxic conditions (Ognalaga & al. 1994, Suzumura & Kamatani 1995, Celi & al. 1999).

All sediment samples collected from the study area were routinely shielded with N_2 during sampling, storage, and extraction for the first two steps. Because P fractions proved to be more sensitive to

storage-induced changes in oxic sediments (**II**), after each sampling cruise, the samples collected from brown surface sediment layers were extracted first and the reduced deep layers last. Generally, all sediment samples were extracted within 3–4 months, but some samples from the deepest reduced layers were stored even longer. According to results for the N_2-shielded reduced samples (**II**, Fig. 2), the storage-induced changes can be considered relatively small. Moreover, it is likely that the possible changes in the actual samples were even smaller than in the test samples, because the containers of the test samples were opened and mixed for subsampling several times during the experiment, while the actual sediment samples were stored undisturbed. Furthermore, excluding the changes in the Fe-bound P in the oxic sample, the changes in P fractions during long-term storage were relatively small compared to concentration differences in the P fractions among different sampling sites (**III**, **IV**, **V**). In conclusion, when using N_2-shielding during sediment sampling and storing, the possible storage-induced changes in P fractions were considered to be small and they were not considered to bias the fractionation results or comparisons of the results from different sampling sites.

In addition to storage-induced changes in P fractions in sediment, the effect of storage and preservation on the extracts was also assessed (**II**). Results suggested that, in general, storage-induced changes in P concentrations were smaller if the extracts were acidified, and that the labile OP fraction (NRP) was among the most sensitive of the forms of P (**II**, Fig. 5). The results also demonstrated that if the extracts are filtered (for PO_4-P), acidified (pH 2), and stored at 5ºC, the determinations can be made with satisfactory results even after one week of storage. However, there was a slight decrease in NRP and HCl-iP, and therefore it is recommended that these fractions are analysed as soon as possible. In this study, the extracts were routinely filtered as soon as possible after extraction, acidified, and analysed for P the following day or within a few days. Thus, the storage of extracts prior to P determination likely did not cause any significant errors in P fractionation results.

4.1.3 Changes in surface sediment P forms from spring to autumn

The sampling cruises were made in spring and in autumn. Thus, the seasonal change in different P forms was studied by comparing P fractionation results of the surface sediments (down to a 5 cm depth) taken from sites GF2F and LL3a in April and in August 2004 (Fig. 3). Temperature in the bottom water (3–5°C, 1 m above the sediment) was similar in both April and August. At the hypoxic site GF2F, O_2 concentration in the near-bottom water (ca. 5 cm above the sediment) did not change (0.8–0.7 ml l^{-1}), while at LL3a, O_2 conditions improved from April (2.4 ml l^{-1}) to August (3.8 ml l^{-1}). The changes in different P fractions were taken into account only if the spring and autumn samples differed by more than 20%, because small variations may be caused by spatial heterogeneity.

Most of the observed changes in the P fractions occurred within the topmost 2-cm layer (Fig. 3). In autumn, the Fe-bound P (NaBD-iP) was markedly lower in the 1-cm surface layer at the hypoxic GF2F site. Loosely adsorbed and pore water P (NaCl-iP) showed a similar distribution pattern. Apparently, the Fe-bound P was released during the continued poor O_2 conditions at GF2F. In contrast, P bound to hydrated oxides of Al was higher in autumn, which indicates that part of the released P was bound into a form not sensitive to reduction. However, it is likely that most of the released Fe-bound P was released to the water column and incorporated into organisms. Similar findings were reported by Andrusch et al. (1992). In fact, deposition of algal detritus can explain the concentration of labile (NRP) and refractory OP (Res-P) being higher at the end of August, because the spring bloom was not over during sampling in April 2004 (Algaline, FIMR). As anticipated, the relatively inert apatite-P did not show marked changes.

Although O_2 conditions in the near-bottom water improved during the summer months at the oxic site, LL3a, the concentration of Fe-bound P was smaller in the topmost 1-cm layer in autumn than in spring (Fig. 3), whereas loosely bound and pore water P showed an opposite change. This result provides evidence for the release of P from Fe-oxyhydroxides. It is likely that labile (in the 1-cm layer) and especially refractory OP, being higher in autumn than in spring, originated in deposited OM (Goedkoop & Pettersson 2000). Degradation of OM, in turn, probably lowered the O_2 concentrations in the sediment surface and, consequently, caused the release of Fe-bound P (as well as PO_4-P originating in OP). As at the hypoxic site GF2F, more P was bound to hydrated oxides of Al at the surface at LL3a in August than in April, while apatite-P did not change.

In conclusion, the assessment of the trends in changes in surface sediment P fractions at hypoxic and oxic sites between spring and autumn demonstrates that changes mainly occur within the first 2-cm layer, which receives the deposited material and reacts mostly to changes in O_2 conditions in the near-bottom water. This is reflected in the increase in OP and decrease in Fe-bound P. As in this study, Jensen et al. (1995) found that between autumn and spring, the biggest changes occurred in the soluble, Fe-bound, and labile OP fractions at the sediment

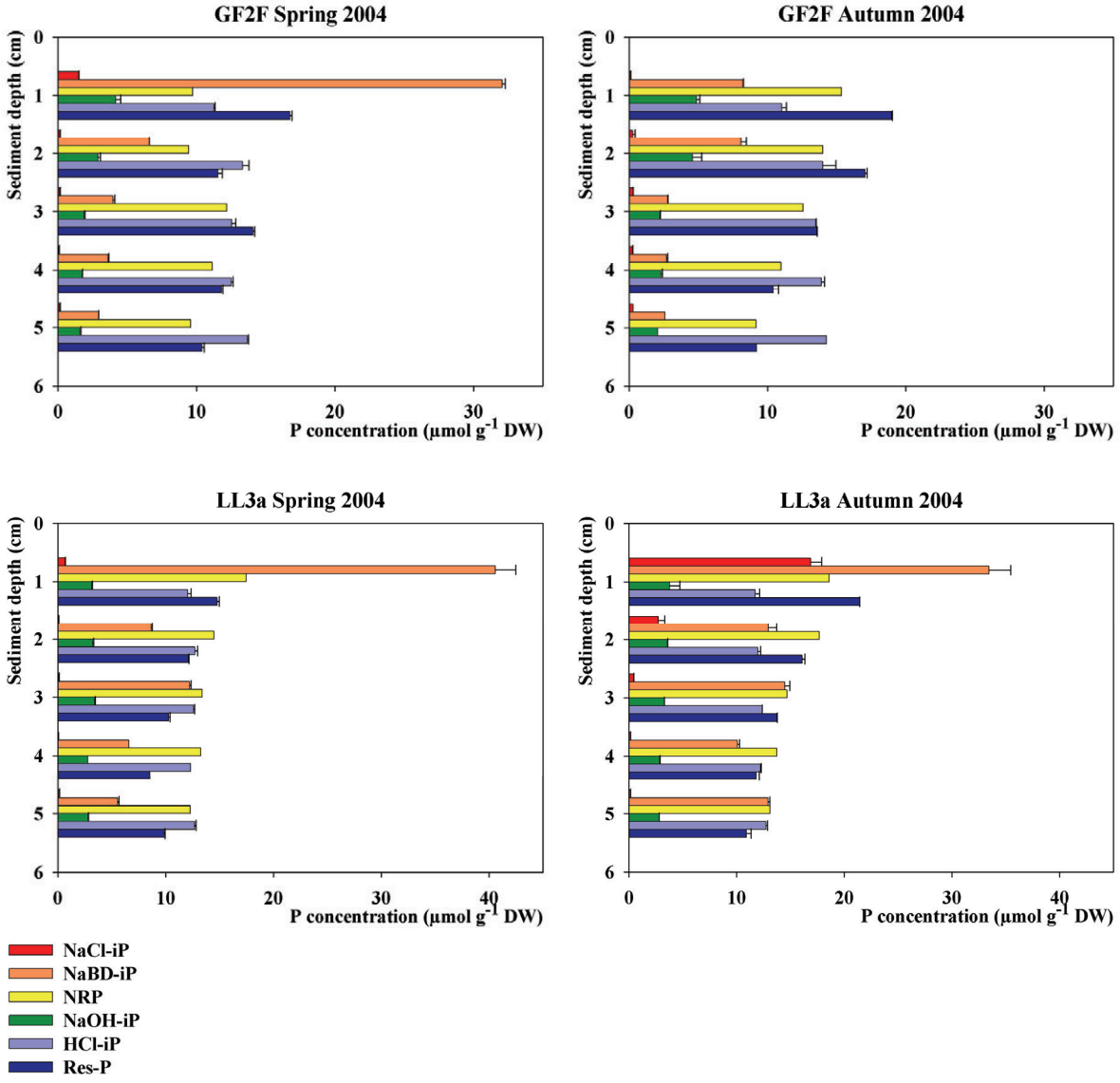


Fig. 3. Changes in P fractions from spring to autumn in hypoxic (GF2F) and oxic (LL3a) sediment surfaces. The y-axis represents sediment depth in cm and the x-axis represents concentration of P in µmol g^{-1} DW.

surface. However, depending on the characteristics of the site, the redox-dependent changes in Fe-bound P can be fast (Krom & Berner 1980) and, depending on changes in O_2 concentration in the near-bottom water and sediment surface, they may have varied markedly during the 4-month study period. If Fe-bound P is released in a dissolved form in reducing conditions, part of if can be resorbed to Al oxides.

4.1.4 Variation in P forms and in their vertical distribution within one sedimentation basin

The chemical distribution of sediment P and its variation within a relatively small sea area was assessed by comparing the P fractions in samples from three different sampling sites located within the same accumulation basin (GF2, Fig. 2). Figure 4 presents the vertical distribution of different P forms in sediments at sites GF2B, GF2F, and GF2K in the central GoF. Sediment accumulation rates vary among the sites, as reported by Vallius (1999b). Sedimentation seemed to be fastest at GF2F and slowest at GF2B. However, when the sediment depths from which the P fractionations were made at a given site were adjusted so that they corresponded to similar sediment units, i.e., they were assumed to be relatively similar by age, the vertical distribution of the P forms was very similar. This distribution pattern reveals that the material being deposited at these sites, as well as the conditions prevailing at the bot-

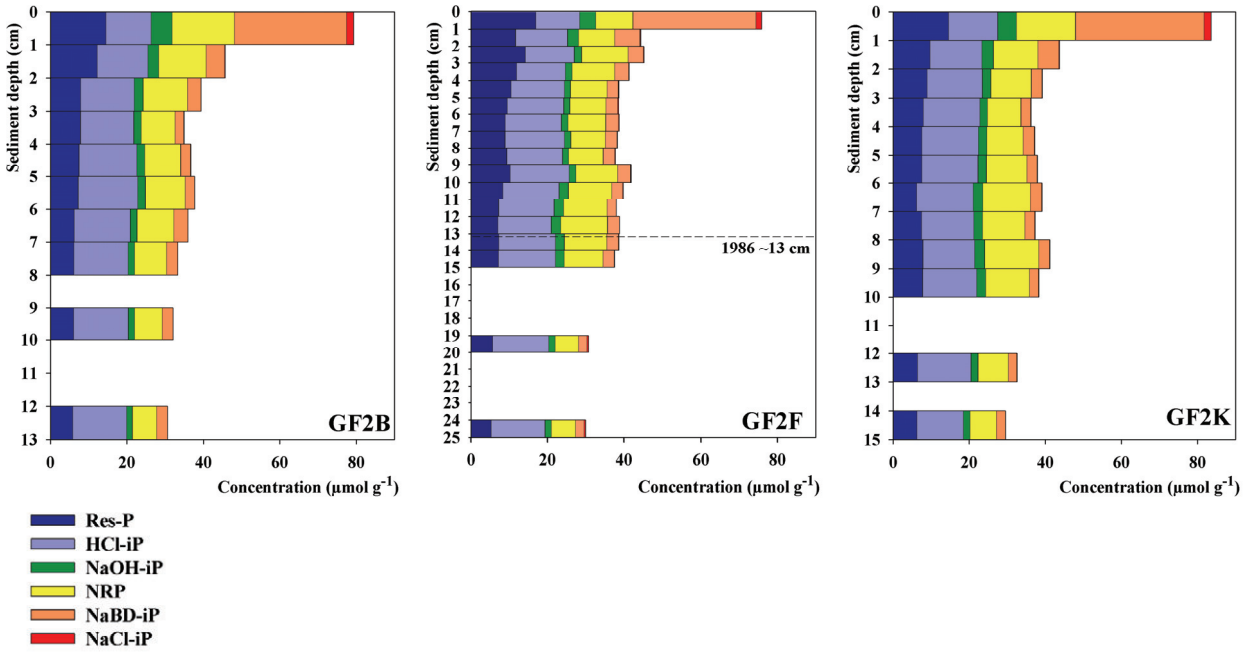


Fig. 4. Vertical distribution of sediment P fractions at three sites located within the same basin in the central GoF. The y-axis represents sediment depth in cm and the x-axis represents concentration of P in µmol g^{-1} DW. The dashed line shows the approximate depth of the ^{137}Cs maximum (i.e., year 1986).

tom during diagenetic processes transforming sediment P, are relatively similar within the basin. This is in accordance with the assumption that the studied basin represents a calm sedimentation environment (Vallius 1999a). In conclusion, although the accumulation rate of sediment (and P) may vary, even within a fairly small area, biogeochemical processes can result in a similar distribution of chemical forms of sediment P in similar, calm sedimentation environments.

4.2 Chemical character of sediment P in relation to sediment properties and chemistry of the pore water and near-bottom water (III, IV, V)

Papers **III**, **IV**, and **V** describe studies on the vertical distribution and chemical character of sediment P in shallow estuaries (**III**), in coastal sediments overlain by oxic near-bottom water (**IV**), and in poorly oxygenated open sea sediments (**V**). The papers attempt to relate the distribution and behaviour of sediment P to the sediment properties as well as the chemistry of the pore water and near-bottom water at each site. This summary further analyses the results by comparing the chemistry and behaviour of sediment P in the different areas and by relating the observed trends to the environmental properties in general.

First, the chemical P fractionation data from the whole study area was analysed statistically to find out whether the chemical character of sediment P differs enough to separate the sites spatially into different groups. A scatterplot in Fig. 5 shows the results (discriminant scores) from discriminant analysis (DA). Different symbols represent data from different areas: estuaries (including sampling sites presented in **III**), coastal areas (sites in **V**, including site XV1), and open sea areas (sites in **IV**, excluding site XV1). The distribution of the three symbols into relatively well-separated groups (Wilks' λ for functions 1 and 2 were 0.121 and 0.803, respectively, and $p < 0.001$), as well as the fact that 89.6% of the originally grouped cases were correctly classified in the analysis, demonstrate that the three study areas differ significantly from each other with respect to sediment P chemistry. In this analysis, site XV1 was assumed to represent a coastal site, because water depth at XV1 was slightly less than 60 m, although the other coastal sites were clearly shallower (Table 1). In fact, Fig. 5 suggests that the group of coastal sites was more variable with respect to their sediment P chemistry than the estuary and open sea sites. This is reasonable because one of the sites was located in a transportation area, one in the AS, and the rest of the sites in the OM-rich eastern GoF (Fig. 2). A closer examination of the analysis (correlation between each P fraction and discriminant functions) revealed that the P bound to hydrated oxides of Fe and Al (i.e., NaBD-iP and NaOH-iP fractions) seemed to be responsible for separating the estuary sites from the others, while the apatite-P (HCl-iP) separated the open sea sites,

and the OP (mostly refractory) the shallow coastal sites. In other words, 1) P bound to oxides of Fe (and other reducible metals) as well as to oxides of Al (and other metals not reduced chemically) is more common in the estuary sediments than in other areas, 2) Ca-bound, mainly apatite-P dominates in poorly oxygenated open sea sediments, and 3) OP is most abundant in the shallow coastal areas overlain by oxic near-bottom water. Because the different binding and solubility forms of P differ in their potential to be buried with the sediment, the spatial distribution of different P fractions provides evidence that the estuaries, shallow coastal areas, and poorly oxygenated open sea areas also differ in their potential for P release from the bottom sediments with time.

In the following chapters the reasons for the spatial distribution of the P fractions as well as its consequences are examined by comparing physico-chemical properties of the sediments and the chemical character of sediment P reserves. Finally, the occurrence of sediment P in its different binding and solubility forms is related to burial and potential for release of sediment P with time in the northeastern BS.

4.2.1 Sediment properties in the study area

The chemical compositions of the sediments in the study area are presented in paper **III** (Table 3), **IV** (Table 3, Fig. 4), and **V** (Table 3, Fig. 4). Table 2 summarises sediment accumulation rates (SAR), water content, and elemental composition in the surface sediment layers (1 cm) and Fig. 6 presents particle size distribution in surface sediment layers.

At the coastal site affected by transportation, C63, and at the shallowest estuary site in Ahla Bay (Ahla2) the surface sediment was coarsest in texture. In contrast, Paila Bay, especially its three innermost sites, was high in clay transported from the clayey watershed. The clayey soils are rich in Fe and Al oxides (Hartikainen 1979, Peltovuori 2006), which was reflected in the fact that the Paila Bay sediments showed the highest Fe and Al concentrations. High transportation of material from the watershed was also reflected by the rather fast sedimentation rates in Paila Bay (Table 2). The variation in SAR within both estuaries, as well as among the coastal and open sea sites is affected by bottom topography (Winterhalter & al. 1981).

Inorganic C being low in the sediments of the research area (Conley & al. 1997, **III**, **IV)**, total carbon (TC) is approximately the same as total organic C (TOC). TC tended always to decrease with sediment depth (**III**, Table 3; **IV**, Fig. 4; **V**, Fig. 4) as a result of degradation of OM, which can continue slowly even deep down in the sediment (Williams & Mayer 1972). Generally, TC was rather high, especially in the inner Gulf, and decreased westwards, especially in the open sea (**IV**, Fig. 7). The highest values (9150–10116 μmol g^{-1}) in the surface sediments were found at the eastern sites. An eastwards increasing trend in TC in the GoF has also been reported by Carman (1998). This is apparently attributable to the inflow of the River Neva and to a high nutrient loading (Grimvall & Stålnacke 2001,

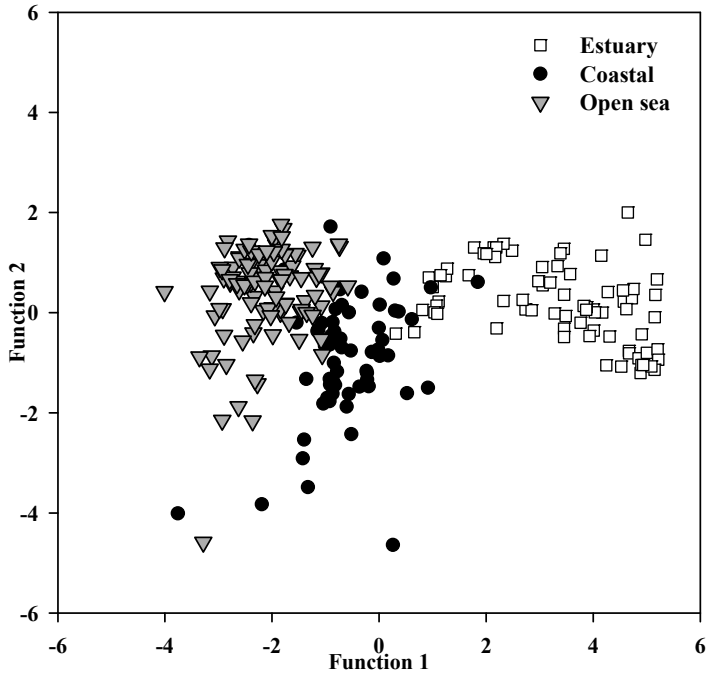


Fig. 5. A scatterplot representing discriminant scores from DA.

Table 2. Sediment accumulation rate, water content, elemental composition, as well as organic C:N and C:P ratios in the surface sediment layers (1 cm). SAR is presented in g m^{-2} y^{-1}, water content (W%) as weight percent, and all concentrations are presented in µmol g^{-1} DW.

Site	SAR	W%	TP	TC	TN	TS	TFe	TAl	TMn	TCa	C:N	C:OP
Paila10	4580*	83	47.2	2024	188	65.9	1139	3544	13.1	218	10.8	148
Paila14	5540*	88	76.1	2555	230	122	1393	3910	17.9	243	11.1	156
AS5	4650*	91	67.8	2763	355	149	1087	2848	13.7	257	7.8	174
AS3	840*	87	59.0	2952	243	105	947	3020	11.9	292	12.2	173
Ahla2	730	91	41.3	4450	321	112	601	2497	9.9	245	13.9	303
Ahla6	660	92	76.3	4138	314	150	830	2869	11.8	291	13.2	208
Ahla9	1373	92	93.1	4429	436	168	813	2597	16.1	239	10.2	210
AS2	900*	89	82.3	5545	640	129	797	2630	18.0	242	8.7	180
C63	-	85	41.2	3821	428	167	567	2268	13.2	299	8.9	229
BISA1	990	96	88.0	9150	1017	396	587	1784	39.6	249	9.0	122
BZ1	430	96	79.9	9179	1082	446	465	1706	27.4	220	8.5	141
AS7	840*	91	41.6	4048	417	340	833	2408	9.9	316	9.7	280
JML	170*	96	46.0	6348	580	382	635	1929	12.6	262	10.9	254
GF1	350*	94	46.1	7432	795	556	691	2293	8.1	270	9.4	273
E3	-	93	49.3	5224	478	603	1107	2532	116	285	10.9	220
GF2B	-	94	91.3	6448	657	338	717	2059	502	255	9.8	209
GF2F	958	93	81.7	6765	650	424	2049	2550	381	443	10.4	253
GF2K	-	92	76.3	6082	603	448	853	2345	320	291	10.1	202
LL3a	329	89	88.4	6261	653	278	821	2462	82.5	234	9.6	194
XV1	330	95	62.7	10116	975	504	634	1810	16.0	209	10.4	160

SAR values labeled with an asterisk (*) are from Mattila & al. 2006.

HELCOM 2003), resulting in severe eutrophication in the eastern GoF (Conley & al. 1997). The sediment in Ahla Bay was higher in TC than that in Paila Bay, which reflects the higher TOC loading in the River Kymijoki than in the River Paimionjoki (HELCOM 1998). In coastal and open sea sediments, the trends in many chemical variables in the surface sediments and in the near-bottom waters seem to follow that of TC (**IV**, Fig 7; **V**, Fig. 7a, 7b). High OM content maintains active mineralisation, which results in consumption of O_2 and production of dissolved nutrients.

Excluding the OM-rich coastal and open sea areas, the spatial distribution of sediment TP (Table 2) did not show trends as clear as that for TC. This results from the fact that sediment P is, to a great extent, comprised of inorganic P forms. The lowest TP concentrations were found at the innermost estuary sites, at the coastal site strongly affected by transportation (C63), as well as in the northern BP and western GoF.

As for TC, TN is supposed to be mostly organic, and its decreasing trend with sediment depth (**III**, Table 3; **IV**, Fig. 4; **V**, Fig. 4) can be attributed to degradation of OM containing N (e.g., Kemp 1971). The slowly degradable and refractory forms become buried, and inorganic forms of N (e.g. some NH_4^+ adsorbed to mineral surfaces) constitute a fairly small proportion of the TN concentration in the sediment (Carman 1998). Accordingly, the spatial distribution of surface sediment TN (Table 2) roughly followed the distribution of TC, being lowest in the estuaries. The easternmost sites, closest to the highest nutrient loading, were richest in TN.

The organic C:N and C:P ratios have been used in assessing the origin of sediment OM. For example, Ruttenberg and Goñi (1997) assumed that in the Amazon River estuary (Brazil) higher ratios indicated a terrestrial origin for the sediment phytodetritus, while a lower ratio indicated a marine origin. In this study, the high organic C:N ratios in the inner Ahla Bay support the conclusion that a high proportion of OM in the surface layers was transported by the river from the drainage area. Generally, the C:N ratios were lowest at the shallow coastal sites, but even there they exceeded the Redfield ratio (C:N:P ratio of 106:16:1; Redfield & al. 1963), which is assumed to indicate the preferential degradation of N (Krom & Berner 1981, Koop & al. 1990) or the terrestrial origin of OM (Ruttenberg & Goñi 1997, Carman 1998). The close proximity of these sites to the shore agrees with the latter conclusion. Sediment C:N ratios higher than the Redfield ratio have been reported previously in the BS e.g. by Koop et al.

(1990), Carman (1998), and Edlund and Carman (2001).

The high organic C:P ratios in the inner Ahla Bay also support the conclusion that there is a high loading of terrestrial OM. Another explanation may be preferential degradation of P (Froelich & al. 1979, 1982, Berner & al. 1993), although Ingall and Van Cappellen (1990) concluded that the ratio strongly depends on the sedimentation rate. It is noteworthy that the organic C:P ratios were higher for the poorly oxygenated open sea sediments than for those from the shallow coastal areas, which agrees with the findings of Ingall et al. (1993), Edlund and Carman (2001), and Virtasalo et al. (2005). This phenomenon was ascribed, for example, to enhanced release of P from the anoxic sediments. Theoretically this is reasonable because PO_4-P groups and inorganic and organic compounds can be bound to oxide surfaces by the same mechanism. Thus, they are prone to being released as a result of reduction of Fe in the sediment (Ognalaga & al. 1994, Suzumura & Kamatani 1995, Celi & al. 1999). The low organic C:P ratios at the TC-rich easternmost sites (Table 2; **IV**, Fig. 7) might be attributable to the high P loading from the inner GoF, but also to the severe eutrophication in the eastern GoF (Conley & al. 1997) leading to deposition of marine OM.

Generally, the sediments of the study area were fairly high in Fe and Al and relatively low in Ca, which is typical of the northeastern BS (Winterhalter & al. 1981). That the peak value of Fe occurred at the sediment surface in the central GoF (GF2F and E3; Table 2) despite the poor O_2 conditions indicates the presence of NO_3-N (Table 1), which maintains the redox potential high enough to keep Fe-oxyhydroxides precipitated (Mortimer 1941, 1971, Froelich & al. 1979). Furthermore, an abundance of total Mn and Ca (Table 2), as well as Ca, Mn, Fe, and Mg in various extractants (Table 4d, given as an appendix), in the surface sediment of the GF2 basin suggests precipitation of some authigenic phase (Ingri & al. 1991, Carman 1998, Neretin & al. 2003). In coastal and open sea sediments, Fe and Mn, enriched as oxides in the oxic layer, usually decreased strongly with sediment depth (**III**, Table 3; **IV**, Table 3; **V**, Table 3; Table 4c–f) as a result of reduction-induced dissolution (Mortimer 1971). In the deepest sediment layers studied, Al, Ca, and TS as well as Fe tended to increase, indicating formation of stable compounds. The concomitant increase in Fe and TS in the reduced layers indicates the formation of ferro sulphides and pyrite (Berner 1970, Pyzic & Sommer 1981, Thamdrup & al. 1994). This reaction pattern affects the P binding by removing Fe from pore water, which hinders the formation of oxyhydroxides in the surface sediment (Krom & Berner 1980, Caraco & al. 1989, Roden & Edmonds 1997, Anschutz & al. 1998). The decrease in TS within the topmost few-cm layers at the easternmost sites (**III**, Table 3; **IV**, Fig. 4; **V**, Fig. 4) can be ascribed to the degradation of S-containing organic compounds and incorporation of the sulphide produced into pyrite (Berner 1970, Jørgensen 1977, Smith & Klug 1981). Furthermore, the presence of white bacterial growth at the open sea sites was linked to the biogeochemistry of S. The bacteria were probably the sulphide-oxidizing *Beggiatoa* sp. (Jørgensen 1977) often found in the GoF (Vallius 2006, Kotilainen & al. 2007) reflecting poor O_2 conditions.

Redox potential varied greatly (ranging from 74 to 439 mV in the near-bottom water and from -218 to 432 mV in the 10-cm sediment layer). Usually, it decreased most strongly within the topmost 1–2 cm layer in the sediments highest in OM (**III**, Fig. 4; **IV**, Fig. 6; **V**, Fig. 6), which agrees with the observations of Mortimer (1971). A redox potential of ca. 230 mV (240 mV, according to Mortimer 1942, 1971) is considered the limit value below which Fe^{3+} is reduced to Fe^{2+}. Theoretically, it is also a limit for dissolution of hydrated oxides of Fe^{3+} and, consequently, for release of Fe-bound P. The higher redox potential below 2-cm depth at some oxic sites (e.g. Ahla2 and AS2) may have been caused by the burrowing activity of benthic animals. The pH ranged from 6.7 to 7.8 (a similar range was also seen in the near-bottom water) (**III**, Fig. 4; **IV**, Fig. 6; **V**, Fig. 6). The reduced conditions also explained the elevated pH at the OM-rich sites (Caraco & al. 1989). The elevated concentration of OH^- ions can result in replacement of PO_4-P from oxide surfaces, which further promotes P release in reducing conditions. In addition, SiO_4-Si competes with PO_4-P for sorption sites on oxide surfaces more efficiently at higher pH, because the anions of weak acids have their sorption maxima in the ligand exchange reaction near their pK_a values, which are higher for silicate than phosphate (Hingston & al. 1967, Ryden & al. 1987).

4.2.2 Spatial and vertical distribution of P and other extracted elements

The discriminant analysis (DA; Fig. 5) suggests that the estuaries, the poorly oxygenated open sea areas, and the shallow coastal sediments overlain by oxic near-bottom waters differed with respect to the six P fractions and other elements co-extracted with P (Table 4a–f). This chapter attempts to relate the P forms with the sediment properties. Figures 7a and 7b give a graphical overview of the vertical distribution of the six P fractions at different locations in the study area (the dotted lines in figures show the approximate depth of the ^{137}Cs maxima, i.e., year 1986). Furthermore, Fig. 2a and 2b in **III**, Fig. 3a and 3b in **IV**, and Fig. 3 in **V** present the P fractionation results combined with available PO_4-P, Fe, and Mn data for the sediment pore water.

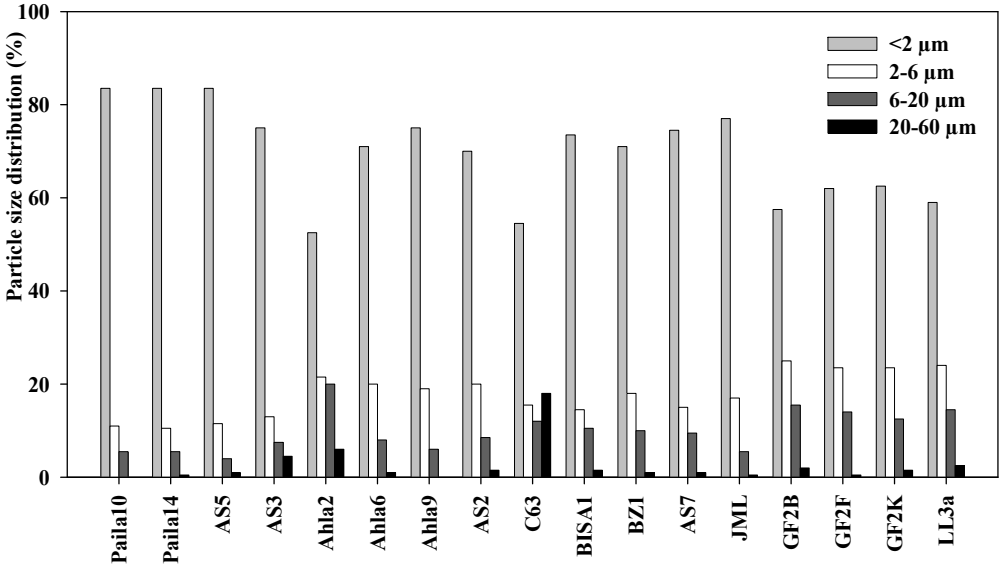


Fig. 6. Particle size distribution in the surface sediment layer (0–1 cm) of each sampling site. The y-axis represents percentual (per weight) portion of each size fraction.

Total extractable P (TP_{extr}) in the sediments was, on average, 45 µmol g^{-1} DW (0.14%), but the 1-cm surface layer showed P enrichment, the average being 67 µmol g^{-1} DW (0.21%). TP_{extr} was highest in the surface sediments at the OM-rich eastern sites (124 µmol g^{-1} DW at maximum) and in the estuaries (especially at Ahla9), while it was lowest in the westernmost open sea sites. The peak values of TP_{extr} are relatively high, although even higher values have been reported in the GoF and in the Gdansk Bay (Carman 1998). A later study (Lukkari, unpublished data) revealed that TP_{extr} values in the Gulf of Bothnia were almost as high as in the GoF.

Generally, inorganic P predominated in the estuaries, in the coastal transportation area, and at the westernmost sites, as well as in the subsurface sediments in the central GoF. In contrast, OP predominated at the three OM-rich easternmost sites, in the AS, and in the surface layers in the western and central GoF (on average 44%, range 14–70%; Fig. 7a, 7b). Carman (1998) proposed that inorganic P is the dominant form in the BS, although Edlund and Carman (2001) reported that OP forms a fairly high proportion of TP in the BP, especially in anoxic areas. In the open sea, OP closely followed TC and had an increasing trend towards the inner Gulf (**IV**, Fig. 7). Generally, OP was most abundant in the topmost 1–3 cm layer, below which it decreased because of mineralisation. The lower OP concentration in estuaries than in coastal and open sea areas can be attributed to the transportation of light, slowly deposited OM by river water towards calmer sedimentation environments.

The vertical distribution of TP_{extr} in the top 25-cm of sediment varied considerably within the whole study area, and also within the three contrasting environments (Fig. 7a, 7b). An almost stable or slightly decreasing trend was found at the innermost estuary sites as well as in the northern BP, whereas in the middle of the Paila Bay estuary the TP_{extr} fluctuated. At the rest of the sites, TP_{extr} decreased with depth. Similar downwards decreasing trends have been described in estuaries (Berner & Rao 1994) and in coastal marine sediments (Krom & Berner 1981, Klump & Martens 1987, Jensen & Thamdrup 1993, Jensen & al. 1995). They are ascribed to degradation of OP and to redox-induced release of Fe-bound P in the deeper sediment layers and its accumulation at the oxidised surface (Mortimer 1971, Berner & Rao 1994). However, several studies on marine sediments have reported almost stable vertical distributions of P (Ruttenberg & Berner 1993, Slomp & al. 1996a,b). This discrepancy may be caused, for example, by different SAR values or mixing of the sediment by benthic animals. In the shallow northeastern BS, the sedimentation of new OP-rich material is so fast that it masks the changes caused by diagenetic transformation of deposited P into its final buried form. Furthermore, OP has less time for mineralisation during deposition in the water column (Hargrave 1975, Carman 1998) than in deeper areas. On the other hand, the smallest SAR value (Table 2), found at the mouth of the GoF (170 g m^{-2} y^{-1}), was close to that reported by Ingall and Jahnke (1994) for the Peru margin and in the Santa Monica Basin.

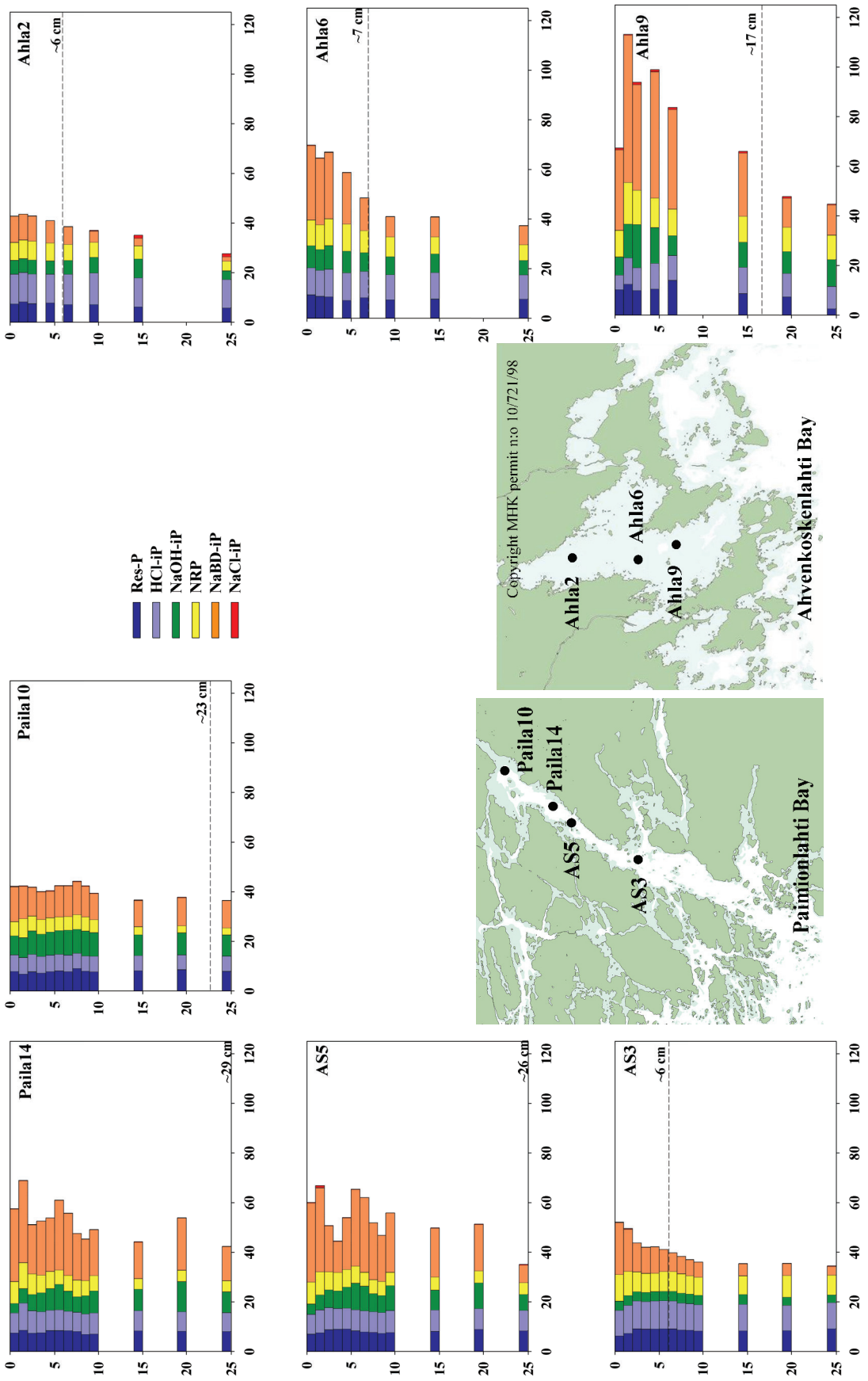


Fig. 7a. Vertical distribution of sediment P fractions in two shallow estuaries in the northeastern BS.

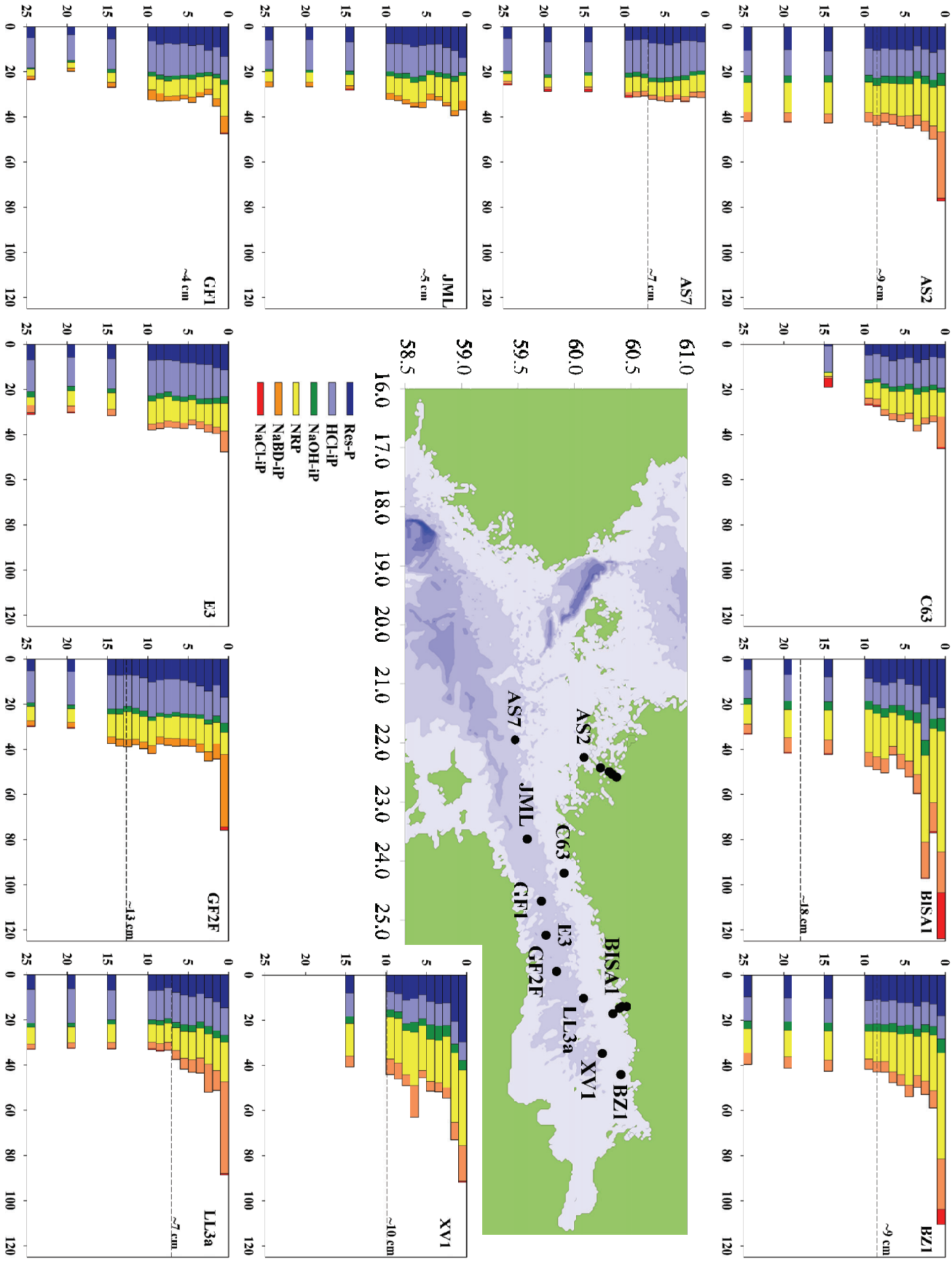


Fig. 7b. Vertical distribution of sediment P fractions in coastal and open sea areas in the northeastern BS.

Sediment accumulation rates (Table 2) varied greatly among the sampling sites, and it seemed to influence strongly the vertical distribution of P, especially in the estuaries. Near the centre of Paila Bay, the high SAR and the variable TP_{extr} distribution suggested temporal changes in the amount of P sedimented (Fig. 7a, 7b). At the innermost site of the estuary, in turn, the stable distribution of TP_{extr} despite the high SAR suggested more stable deposition. In the innermost site of the Ahla estuary, in contrast, transportation of fine particulate material (Fig. 6) resulted in low SAR (Table 2) and a rather stable vertical distribution of TP_{extr}. If the sedimentation rate is low or if the OM is highly degraded, there will be less P transfer to other forms (e.g. in the northern BP). In addition to SAR and the quality of deposited material, mixing of sediment layers by deep-burrowing benthic animals may affect the vertical distribution of P forms. In the present study, the traces of bioturbation in the subsurface layers of most of the sediment cores suggested that bioturbation may have occurred during oxic conditions.

4.2.2.1 Immobile P

Immobile forms of sediment P separated by the P fractionation method include P bound to hydrated oxides of Al (or other metals not reduced in the previous step; NaOH-iP), Ca-bound, mainly apatite-P (HCl-iP), and refractory OP (Res-P). These forms, assumed to be buried with sediment and removed from the nutrient cycle, were mostly relatively stable with sediment depth. Immobile P (26–81% of TP_{extr}) predominated over reactive P in the whole 25-cm section at the innermost estuary sites and at the westernmost open sea sites. At the estuary sites with the highest SAR values, in turn, immobile P was higher than reactive P only in the deepest sediment layers. At the rest of the estuary sites, immobile P generally slightly predominated over reactive P below the surface layers. Similar findings have been reported, for example by Coelho et al. (2004).

Aluminum-bound P. P bound to hydrated oxides of Al (NaOH-iP) via ligand exchange reactions formed 2–24% of TP_{extr} in the northeastern BS. This P form is relatively stable in sediment (Jensen & Thamdrup 1993, **II**), and its concentration varied only a little with sediment depth (Fig. 7a, 7b). Not being redox-sensitive, the Al-bound P is important for burial of P (e.g. Kopáček & al. 2005), especially in the hypoxic sediments common in the northeastern BS. Its proportion was highest in the estuary sediments (maximum 17.5 μmol g^{-1} DW at Ahla9) and lowest in the deepest layers of the open sea sediments. The concentration of Al-bound P was close to that of Fe-bound P in the inner estuaries and in deep sediment layers at other sites. Because the Al concentration is relatively high in the northeastern BS (especially in the northern BS; Lukkari, unpublished data), it is likely that sediment Al plays a role in P burial in this environment. In fact, in the Delaware Estuary (USA), almost as high a proportion of P was found to be associated with Al- as with Fe-oxides (Lebo 1991). However, Forsgren and Jansson (1993) concluded that Fe is more important in P binding than Al in the River Öre Estuary, BS. The spatial distribution of Al-bound P in the study area is in accordance with the assumption that it originates from river transported, clayey-rich erosion material (Fig. 7a, 7b). In the estuaries studied, the eroded material is expected to be rich in clay particles coated by poorly crystallised oxides of Al and Fe (Hartikainen 1979, Peltovuori 2006), which are effective in P binding (Barnhisel & Bertsch 1982). A similar outwards decreasing trend of Al-bound P was reported, for example, in the Mondego Estuary (Portugal; Coelho & al. 2004). The hypothesis that the NaOH-iP originated in clayey material was supported by the fact that concentrations of NaOH-extractable Al decreased from the inner to outer estuary in Paila Bay, were lower in coastal and open sea sediments than in the estuaries, and were higher in Paila Bay than in Ahla Bay, which was lower in Al and clayey material. On the other hand, the abundance of alkali-extractable Al and Fe at the OM-rich eastern sites can be ascribed to humic matter that forms complexes with Al^{3+} and Fe^{3+} (Schnitzer 1969, Gerke & Hermann 1992).

It is possible, however, that alkali extraction also released some Fe and Fe-bound P from oxides because of incomplete reduction with dithionite (**III**). The poorly crystallised naturally occurring oxides of Fe and Al in the sediments are probably mixtures rather than pure compounds. Alkali extracted rather high concentrations of silica that was mainly biogenic, as suggested by its enrichment in the OM-rich sediments. Furthermore, an abundance of diatoms in the sediments of the eastern coast of the GoF has been reported previously (Vallius 1999a). Some of the NaOH-extractable Si may have also been inorganic and released from Al-oxide surfaces. In that case, the abundance of alkali-extractable Si suggests the potential for competition with P for binding surfaces in the eastern GoF (Ryden & al. 1987, Hartikainen & al. 1996, Koski-Vähälä & al. 2001).

Calcium-bound and apatite-P. The proportion of Ca-bound and apatite P (HCl-iP) of sediment TP_{extr} varied from 4 to 60%. This P form was lowest at the organic-rich eastern coastal sites, and its highest concentrations (15.9 μmol g^{-1} DW) were found in the central GoF (Fig. 7a, 7b). However, when related to the TP_{extr}, apatite-P was most abundant at the coastal site as well as at the site in the inner estuary of Ahla Bay, which were most affected by sediment transportation. A similar enrichment of apatite-P in transportation-affected lake sediment was reported by Williams et al. (1976) and by Forsgren and Jans-

son (1993) and Lopez (2004) in shallow parts of estuaries. The enrichment of apatite-P at the transportation-affected coastal site was in accordance with the high Ca concentration, coarse particle size (Fig. 6), and low TC in the sediment (Table 2). Furthermore, the spatial difference between apatite-P and organic sediment constituents was evident: apatite-P decreased from the northern BP (AS7) towards the OM-rich (and Ca-poor) inner Gulf (**IV**, Fig. 3a, 3b).

In addition to Al-bound P, apatite-P was among the most stable P forms in the sediments, especially in the estuaries, as also reported by Salomons and Gerritse (1981) and Jensen et al. (1995). In contrast, apatite-P seemed to increase with sediment depth in the open sea sediments, especially in the western GoF. The concomitant decrease in refractory OP suggests that this increase may result from formation of some P-containing authigenic minerals (Williams & Mayer 1972, Ruttenberg 1990, Ruttenberg & Berner 1993, Delaney 1998), although in this study, the authigenic apatite P was not distinguished from detrital apatite-P. Virtasalo et al. (2005) separated these two apatite groups in the surface sediments in the AS, and from his results it can be calculated that ca. 8–12% of TP_{extr} was authigenic, while ca. 27–35% was detrital apatite-P. It can be anticipated that the detrital apatite-P is higher in the estuary sediments than in the coastal areas. According to our recent study, authigenic apatite-P is slightly more abundant in sediments of the western open GoF than in the AS (Lukkari, unpublished data).

Refractory OP. The refractory OP fraction (Res-P), which mainly represents P in refractory humic material, formed 4–38% of sediment TP_{extr} in the whole study area. It was lowest at the coastal site affected by sediment transportation and highest in the organic-rich eastern GoF (peak value 29.7 µmol g^{-1} DW). Thus, its spatial distribution seemed to be dictated by OM as well as transportation of fine particulate OM. Accordingly, the refractory OP followed the trends of TC and TN, increasing towards the east in the GoF (**IV**, Fig. 7). The vertical distribution of refractory OP, assumed to be immobile, varied among the sampling sites. It showed a stable distribution pattern in the estuary sediments (similar to that seen in the Öre River estuary; Forsgren & Jansson 1993), in the northern BP, in the AS, and at the transportation-affected coast, but in the open GoF and especially in the organic-rich eastern GoF it diminished with sediment depth. The decrease can be attributed to two factors: 1) gradual degradation of slowly degradable OP compounds and/or 2) increased SAR (e.g., Kemp 1971, Jonsson & Carman 1994, Emeis & al. 2000) during the past decades.

The molecular composition of OP is complex and the components are largely unidentified (Hedges & al. 2000, Quiquampoix & Mousain 2005). In this fractionation method, labile OP is separated from refractory OP on the basis of its solubility in alkali. However, refractory OP contains compounds that can degrade with time, and labile OP also contains stable and slowly degradable compounds. Marine microorganisms are able to utilise refractory OP (Benitez-Nelson & al. 2004), and the tendency for refractory OP to decrease relatively deep in the sediment, found in several studies, suggests that mineralisation processes can occur slowly for a long time (e.g. Williams & Mayer 1972). Furthermore, ^{31}P-NMR studies have shown that half-lives of some types of OP compounds in aquatic sediments are about one or two decades (Ahlgren & al. 2005, Reitzel & al. 2007). Phosphate released from refractory OP can be incorporated into sediment bacteria (e.g., Gächter & al. 1988) or transformed into some other solid phase P fraction, e.g. incorporated into authigenic minerals. In other words, P may show sink-switching (Froelich & al. 1982, Ruttenberg & Berner 1993, Delaney 1998), instead of being released to the water column. Because of the possibility of such inter-sediment transformation reactions, the decrease in refractory OP was not taken into account in calculating the P efflux estimates.

The increase in SAR, which is another possible explanation for the decreasing trend in refractory OP, as well as in labile OP, is difficult to prove from the data available in this study. Comparison of the depths of ^{137}Cs peak values, i.e., the year 1986, (Fig. 7a, 7b) with the decreasing trends in amounts of forms of OP revealed that, especially in the eastern GoF, the decrease often levelled out at about the sediment depth representing material roughly 20 years old. This suggests that sedimentation has increased during the past 20 years. In fact, according to Emeis et al. (2000) sedimentation has increased in the Gotland Basin, BP, during the past ca. 50 years, and according to Vaalgamaa and Conley (2008) sedimentation has increased in some of the small shallow bays on the northern coast of the GoF during recent decades. However, the P fractionation results show that the sedimentation of the other immobile P forms, apatite-P and Al oxide-bound P, has not increased in the study area during the last ca. twenty years. Thus, if sedimentation of P has increased, it only seems to concern OP forms. This may be connected to eutrophication and increased production of OM in general (Jonsson & Carman 1994, Vaalgamaa & Conley 2008), especially in the eastern GoF.

4.2.2.2 Reactive P

Reactive P forms (loosely adsorbed and pore-water P (NaCl-iP), P bound to hydrated oxides of Fe (and other chemically reducible metals; NaBD-iP), and labile OP (NRP)) represent sediment P that is or may become available for bacteria and algae and other aquatic organisms in biogeochemical proc-

esses, e.g., by reduction-induced release of PO_4-P from Fe-oxyhydroxides or by degradation of OP into small organic molecules and PO_4-P (Krom & Berner 1981, Berner & Rao 1994). Generally, concentrations of reactive P forms decreased with sediment depth, indicating their loss from the sediment or incorporation into more stable P forms. As the immobile P forms are relatively stable, the vertical distribution of reactive P forms determines the vertical distribution pattern of TP_{extr} in the sediment.

Reactive P formed 19–74% of TP_{extr} in the study area. The proportion was lowest in the northern BP and in the western open GoF, and highest at the OM-rich sites on the eastern coast, followed by the outer estuary sites. In contrast, at the innermost estuary sites, as well as at the westernmost open sea sites, reactive P was not the predominant form at any sediment depth. At the rest of the sites, it usually predominated in the surface sediment layers. The vertical distribution of P fractions (Fig. 7a, 7b) shows that some reactive P was always present also in deep sediment layers (as found in several other studies, e.g., Jensen & Thamdrup 1993, Jensen & al. 1995). These forms may be physically trapped beneath newly depostied material before transformation into their final buried forms, or some of the immobile P forms may have been transformed into reactive P forms within the sediment. Nevertheless, the buried part of reactive P at each site was taken into account when calculating the efflux of P from its sedimentary reserves (see below).

Loosely adsorbed and pore water P. The pore water P and loosely adsorbed P was clearly the least abundant sedimentary P form. Its proportion of TP_{extr}, usually <3%, was the same as that reported in earlier studies (a few percent of TP_{extr}; Pettersson & al. 1988, Jensen & Thamdrup 1993, Jensen & al. 1995). Loosely adsorbed and pore water P was often below the detection limit and it exceeded 3 μmol g^{-1} DW only in three samples: in the deepest layer at the coastal transportation site and in the surface layers at the OM-rich eastern coastal sites. An exceptionally high concentration (20.5 μmol g^{-1} DW) was detected at the surface of the OM-rich BISA1 site. Despite its generally low concentration, NaCl-iP plays an important role because it can diffuse from pore water to near-bottom water and is immediately available for algae and bacteria (Van Eck 1982). Furthermore, loosely adsorbed and pore water P was often highest in the topmost fluffy sediment layer that can be easily resuspended in the near-bottom water. The abundance of this P form is indicative of a lack of free sorption sites for PO_4-P, which can result from dissolution of Fe-oxyhydroxides in reducing conditions and from highly occupied sorption surfaces, or from competition with other anions, such as silicate and organic anions, for sorption sites (Hingston & al. 1974, Ryden & al.1987, Hartikainen & al. 1996, Koski-Vähälä & al. 2001). Boström and Pettersson (1982) also reported a high concentration of soluble P in OM-rich lake sediments saturated with P. The peak concentration of the soluble P at BISA1 was in agreement with the high incubation-derived PO_4-P flux at this site (Table 1). This phenomenon is discussed further below.

Iron-bound P. In the whole study area, P bound to hydrated oxides of Fe (and other reductant-soluble metals; NaBD-iP) formed 4–53% of TP_{extr} and showed a high level of spatial variability. The highest proportions were found in the estuary sediments (the peak concentration, 59.4 μmol g^{-1} DW, was found in Ahla Bay). The lowest proportions were detected in the reduced sediments at the westernmost open sea sites which have, according to the monitoring data of FIMR, often suffered from poor O_2 conditions. Fe-bound P was also relatively low in the apatite-P-rich coastal area affected by transportation of fine particulate sediment that is often high in poorly crystallised Fe oxides (and Al oxides). A spatial difference in the distribution of Fe-bound P and Ca-bound P is also reported by Berner and Rao (1994) for the Amazon River estuary. In the mud sediments, the oxic layer is usually only several millimetres deep (Mortimer 1971, Thamdrup & al. 1994, Conley & al. 1997). Thus, Fe-bound P and reductant-soluble Fe were usually highest in the oxidised surface sediment layers and decreased with sediment depth, the decrease being steepest right below the sediment surface (Fig. 7a, 7b; Table 4a–f). This distribution pattern results from the dissolution of ferric-iron in reduced sediment and the concomitant release of Fe-bound P. The dissolved forms diffuse upwards in the sediment pore water until, at the oxidised surface layer, Fe^{2+} is oxidised and becomes able to bind PO_4-P as ferric-oxyhydroxides. Similarly, Mn dissolves in subsurface sediment (at a higher redox-potential than Fe) and accumulates in surface sediments as Mn oxides (Mortimer 1971, Krom & Berner 1980, Sundby & al. 1992, Thamdrup & al. 1994). In the poorly oxygenated GF2 basin in the central GoF, the abundance of reductant-soluble P and Fe in the surface sediment layers seemed to be attributable to the presence of NO_3-N in the near-bottom water (Table 1), which retarded the reduction of Fe^{3+} (Mortimer 1941, 1971, Froelich & al. 1979, Boström & al. 1982, Andrusch & al. 1992). Furthermore, the abundance of reductant-soluble Si in the surface sediment of this basin suggests that it might enhance the release of P through competition with PO_4-P for sorption surfaces (Hingston & al. 1967, Ryden & al. 1987, Hartikainen & al. 1996, Koski-Vähälä & al. 2001).

Although Fe-bound P was generally most abundant in surface sediment layers, the reductant solution always also extracted some Fe and Fe-bound-P from deep sediment layers. This P form was particularly abundant in the deep layers of the estuary sediments. Similar findings have been reported in

many earlier studies (Balzer 1986, Lovley & Phillips 1986b, Andrusch & al. 1992, Jensen & Thamdrup 1993, Ruttenberg & Berner 1993, Slomp & al. 1996a, Hyacinthe & Van Cappellen 2004). Several possible explanations for this finding can be found in the literature: 1) the reducing agent in the procedure may have a higher reducing power than the natural conditions in sediments, leading to disruption of more crystalline Fe-oxides (Bauwin & Tyner 1957, Mehra & Jackson 1960, Williams & al. 1971a, Ruttenberg 1992, Jensen & Thamdrup 1993); 2) microbial reduction of ferric-iron can be interfered with by adsorbed ligands such as humic compounds (Shukla & al. 1971, Slomp & al. 1996a) or by an abundance of ferro-iron (Hyacinthe & Van Capellen 2004) on oxide surfaces; 3) the presence of ferric-iron in deep sediments may also result from the presence of mixed compounds of Fe^{3+} and Fe^{2+}, which are resistant to reduction in sediment (Lovley & Phillips 1986b); 4) the NaBD-reagent may release some P from Al-oxide surfaces because of the bicarbonate solution (Olsen & al. 1954, Kamprath & Watson 1980) or it may disrupt some hydrated Al oxides and release some Fe present in them as impurities (Williams & al. 1971a, Agbenin 2003) although, in the present study, the Al concentration was relatively low in the NaBD-extracts; 5) finally, the reaction pattern may be related to the release of occluded P in the dithionite reagent (Chang & Jackson 1957, Mehra & Jackson 1960, Williams & al. 1971a, Agbenin 2003). The presence of occluded Fe-compounds has also been suggested to be the reason for overestimation of the microbiological reduction of ferric iron (Hyacinthe & al. 2006). The fact that Fe-bound P and, thus, probably ferric-iron, was much more abundant in the estuary sediments than in the sediments of the coastal and especially open sea areas can result from a high SAR and agrees with the findings by Hyacinthe and Van Cappellen (2004) that ferric-iron removal via sulphate reduction and formation of ferro-sulphides is less efficient in estuary sediments than in open sea sediments (see also Caraco & al. 1989, 1990, Thamdrup & al. 1994, Gunnars & Blomqvist 1997). The burial of ferric-iron with adsorbed P in the studied estuaries is an important phenomenon because it removes part of the river-transported P before it can enter coastal and open sea areas.

Labile OP. ^{31}P-NMR studies have shown that the labile OP fraction (NRP) dissolved in alkali includes pyrophosphate, polyphosphate, orthophosphate monoesters and orthophosphate diesters (Ingall & al. 1990, Carman & al. 2000, Hupfer & al. 1995, 2004, Ahlgren & al. 2005, Reitzel & al. 2006). The proportion of labile OP of TP_{extr} (range 8–43%) was smallest in the estuary sediments high in eroded material (Paila Bay) and at the coastal site affected by sediment transportation. Generally, this fraction was highest at the easternmost organic-rich sites (peak value 53.4 μmol g^{-1} DW at BISA1). The increase in labile OP as one moves from the estuaries to the coastal areas, especially in the eastern GoF, could indicate transportation of OP from the terrestrial environment or higher nutrient loading and production of OM in the eastern GoF. The labile OP was relatively stable and decreased only slightly with depth in the estuary sediments and in the northern BP, but a strong decrease was seen in the organic-rich sediments in the eastern GoF (Fig. 7a, 7b). These contrasting trends can be explained by differences in the nature and degradability of OM from inner estuaries to coastal and open sea, as discussed by Martens and Goldhaber (1978) and Stepanauskas et al. (2002). Teichoic acids are fairly stable in brackish sediments and orthophosphate monoesters degrade relatively slowly, while some orthophosphate diesters (e.g., phospholipids and DNA) and especially polyphosphates and pyrophosphate degrade faster (Ahlgren 2006). The stability of this P fraction in the estuary sediments indicates the degradability to be slow relative to the high SAR, leading to high burial of NRP. This feature may result from the terrestrial origin and recalcitrant nature of NRP. It is also possible that the oxic conditions favor the binding of OP compounds on metal oxides transported to the estuaries with eroded clay material. Retention on oxides has been used as an explanation for the slower degradation of OP compounds in oxic than in anoxic sediments (Ognalaga & al. 1994, Suzumura & Kamatani 1995, Celi & al. 1999, Rydin 2000). The clearest spatial trend was the increase in labile OP on moving from the poorly oxygenated northern BP to the organic-rich eastern GoF (Fig. 7a, 7b; **IV**, Fig. 7). The stability of the refractory OP in the northern BP can be explained by the fact that the deposited OM is mainly marine in origin and it has lost its easily degradable forms during transportation and settling. In the inner Gulf, in contrast, the shallowness and closeness to the shore favoured the transportation of terrestrial material of a more recalcitrant nature. However, the strongly decreasing trend in amounts of labile OP with sediment depth in the eastern GoF, if not solely caused by a possible increase in SAR, suggests degradation of OP deposited in the shallow, eutrophied sea area.

4.2.3 Impact of sediment properties on the chemistry of the sediment-water interface

The composition of sediment P and other sediment properties were reflected in the dissolved species of the near-bottom water and pore water at the different sampling sites. In agreement with the classical theory that the binding of P is more efficient in oxic sediments than in anoxic ones (Einsele 1936, 1938, Mortimer 1941, 1942), the concentration of PO_4-P in the near-bottom water (Table 1) was roughly inversely related to the dissolved O_2. How-

ever, some exceptional sites were discovered. At the estuary site AS5 in Paila Bay the near-bottom water was low in PO_4-P and the incubation-derived PO_4-P flux was negative despite a relatively low O_2 concentration. At the eastern coastal organic-rich sites, on the other hand, the near-bottom water was relatively high in PO_4-P and the incubation-derived PO_4-flux was highly positive despite oxic (O_2 >2 ml l^{-1}) near-bottom water. A closer examination of the biogeochemistry in the sediment-water interface explained the binding and release of P at these sites.

At the hypoxic estuary site (AS5), the high NO_3-N in the near-bottom water and sediment-water interface kept most of the Fe precipitated as ferric-oxyhydroxides at the sediment surface (Table 1, Table 4a, Fig. 7a) (Mortimer 1941, 1971, Froelich & al. 1979, Boström & al. 1982). The sediments of the Paila Bay were high in Fe, and a strong concentration gradient in the pore water drove the dissolved Fe from the reduced sediment layers upwards to the oxic layers where P binding to Fe-oxyhydroxides kept the pore water PO_4-P low in the sediment-water interface (**III**, Fig. 2a, Fig. 7a). In addition, hydrated oxides of Al, not sensitive to redox-changes, may have participated in P binding. As a result of these reactions, the incubation-derived PO_4-P flux was directed from near-bottom water to the sediment (i.e., was negative; Table 1). Thus, during sampling, this estuary site acted as a sink for P, despite the low O_2 concentration in its near-bottom water.

An opposite reaction pattern was found at the eastern coastal sites BISA1 and BZ1 where the organic-rich sediments were overlain by oxic near-bottom water (Table 1), but showed a positive incubation-derived PO_4-P flux. A strong concentration gradient and an abundance of NH_4-N in the near-bottom water suggest active degradation of OM and release of nutrients (Martens & Goldhaber 1978, Krom & Berner 1981, Klump & Martens 1987). This process consumes O_2, and may create reducing conditions in the sediment surface layer, although the near-bottom water is oxic (Holdren & Armstrong 1980, Maher & DeVries 1994, Conley & Johnstone 1995). The redox-potential at BISA1 (**V**, Fig. 6) showed that conditions were clearly reducing even in the topmost sediment layer, and the black colour of the sediment suggested the presence of ferro-sulphides (Berner 1970). This agrees with the positive incubation-derived P flux being exceptionally high (Table 1). Although some P bound by Fe-oxyhydroxides was still present in the surface sediment (Fig. 7b, Table 4f), the abundance of loosely adsorbed and pore water P (i.e., NaCl-iP fraction) provides evidence that the ability of the sediment to retain P was low. In addition to poor O_2 conditions, the presence of silicate (Table 1, Table 4f) and other competing anions, e.g. organic acids (Hingston & al. 1967, Ryden & al. 1987), might diminish P binding capacity at the organic-rich sites.

At the other organic-rich coastal site, BZ1, the sediment properties and O_2 conditions were very similar to those at BISA1. However, the incubation-derived PO_4-P flux was about six times lower than at BISA1, although on the basis of the concentration gradient of pore-water PO_4-P at the sediment-water interface an opposite pattern could have been expected (**V**, Fig. 2, Fig. 3). One explanation for the release of sediment P being lower at this site than at BISA1 was the higher NO_3-N concentration in the near-bottom water at BZ1 (Table 1). The presence of NO_3-N hinders reduction-induced dissolution of Fe^{3+} from hydrated oxides (Froelich & al. 1979, Boström & al. 1982, Andrusch & al. 1992). In fact, the reductant-soluble P and Fe at the sediment surface being higher at BZ1 than at BISA1 (Fig. 7b, Table 4f) is evidence for the presence of reactive Fe-oxides at BZ1. Furthermore, the smaller soluble P fraction at BZ1 proves that Fe-oxyhydroxides were able to bind upward-diffusing PO_4-P more efficiently, resulting in lower P release. Both of these sites were higher in OP than in Fe-bound P in the sediment. Thus, it is likely that a considerable part of PO_4-P released from the sediment originated in OP compounds.

Because of the highly heterogeneous nature of the bottom sediments, unavoidable inaccuracy in various measurements, and relatively fast redox-reactions affecting behaviour of P on a relatively short time scale, all the determinations cannot be expected to be in agreement with the theoretical behaviour of the dissolved species in the prevailing conditions. For example, many poorly oxygenated sites in the central GoF, with relatively high PO_4-P in the near-bottom water, showed very different incubation-derived PO_4-P fluxes, even within the same basin (Table 1). Furthermore, benthic fauna, when present, can cause drastic changes in concentrations of dissolved species at the sediment-water interface (Petr 1977, Holdren & Armstrong 1980, Aller 1988).

4.3 Sedimentation, burial and potential for release of P from sediment reserves in the northeastern BS (III, IV, V)

4.3.1 Sedimentation and burial of P in the northeastern BS

In the study area, sedimentation of P varied from 6.3 to 319 mmol P m^{-2} y^{-1} (Table 3, Fig. 8). Generally, it reflected sediment accumulation rates (i.e., SAR values; Table 2), being high in the estuaries (144 mmol P m^{-2} y^{-1}, on average) and in the coastal areas (average 80 mmol P m^{-2} y^{-1}) not highly affected by sediment transportation, as well as in the deep GF2 basin in the central GoF. In contrast, sedimentation of P was lowest at the westernmost

Table 3. Sedimentation and burial of P, minimum estimate of long-term average for annual P efflux, and burial efficiency of total P in the sediment surface at different sampling sites.

Site	Sedimentation of P		Burial of P		Long-term average for minimum P efflux		Burial efficiency
	mmol $m^{-2}y^{-1}$	mg $m^{-2}y^{-1}$	mmol $m^{-2}y^{-1}$	mg $m^{-2}y^{-1}$	mmol $m^{-2}y^{-1}$	mg $m^{-2}y^{-1}$	%
Paila10	193	5992	165	5120	1.7	51.3	85
Paila14	319	9880	209	6481	6.5	200	66
AS5	280	8656	146	4517	7.9	244	52
AS3	43.9	1359	31.3	969	0.7	22.9	71
Ahla2	31.3	969	28.2	873	0.2	5.3	90
Ahla6	46.1	1428	33.9	1051	0.7	21.0	74
Ahla9	92.6	2867	62.7	1941	1.7	51.5	68
AS2	69.6	2156	39.5	1222	1.8	54.9	57
BISA1	123	3802	50.9	1575	4.0	124	41
BZ1	47.5	1472	22.6	699	1.4	42.9	48
AS7	26.5	820	24.5	760	0.1	3.6	93
JML	6.3	195	5.6	173	0.04	1.3	89
GF1	16.6	515	12.1	376	0.3	8.2	73
GF2F	72.7	2252	46.0	1424	1.5	46.0	63
LL3a	29.2	904	14.5	449	0.8	25.3	50
XVI	30.3	939	22.3	691	0.4	13.8	74

sites of the open GoF and in the northern BP (on average, 31 mmol P m^{-2} y^{-1} in the open GoF). The P sedimentation was within the range determined by Kamp-Nielsen (1992) (226–1679 mmol m^{-2} y^{-1}; gross sedimentation) for the Roskilde Fjord (Denmark) only in Paila Bay estuary. At most of the coastal and open sea sites, on the other hand, P sedimentation was relatively close to values reported by Jensen et al. (1995) for the shallow Aarhus Bay (Denmark) (51–63 mmol m^{-2} y^{-1}) and by Baltzer (1986) and Struck et al. (2004) for the Kiel Bight and the Gotland Basin (BS), respectively.

The vertical distribution of P forms revealed that, although the reactive P decreased with sediment depth, some reactive P was always found in the deep sediment layers. Thus, to get more reliable values for burial flux estimates, the buried part of reactive P was summed with immobile P forms in the surface sediment. At each site, the concentration of the reactive P in a sediment sub-sample representing the depth layer closest to the depth of the ^{137}Cs maximum (i.e., the year 1986) was used as a reference value, or a "site specific background value" (see also Hyacinthe & al. 2006) for buried reactive P. This allows the comparison of results from different areas where the ages of the analysed sediment sections differed.

In the northeastern BS, the burial of the total P in the sediment surface varied from 5.6 to 209 mmol m^{-2} y^{-1} (Table 3). The burial was highest in Paila Bay estuary and lowest at the mouth of the GoF. Spatially, it roughly followed the P sedimentation values. The average values in the two estuaries, shallow coastal areas, and open sea areas were 97, 38, and 21 mmol P m^{-2} y^{-1}, respectively. They were higher than the P burial rate estimated for the Aarhus Bay (Denmark) (18 mmol m^{-2} y^{-1}; Jensen & al. 1995) and for the offshore areas on the BP (about 11 mmol P m^{-2} y^{-1}; Carman & Cederwall 2001). In this study, the P burial rate in the shallow coastal sediments was also higher than that recorded by Carman et al. (1996) in the Gulf of Riga (BS). In addition, the burial flux of P recorded by Louchouarn et al. (1997) in the Gulf of St. Lawrence was lower than P burial in the central and eastern parts of the open GoF. The lowest P burial value, which was found at the mouth of the GoF, however, was close to the values determined at the Peru margin and Santa Monica Basin (Ingall & Jahnke 1994). Filippelli (2001) stated that common burial rates for P in continental margin sediments vary between 5 and 80 mmol m^{-2} y^{-1}. In the present study, this range was exceeded only in the Paila Bay estuary. However, in the study of Filippelli (2001) in the Saanich Inlet (British Columbia), the long-term

burial rates for reactive P varied from 100 to 600 mmol m^{-2} y^{-1}, a relatively broad range compared to the values found in the northeastern BS.

The highest burial efficiency of total P in the sediment surface in the study area (93%) was found at the apatite-P-rich site in the northern BP (Fig. 8). This means that in this sea area, most of the P in the sediment surface layer will be removed from the nutrient cycle. Generally, the westernmost open sea sites high in apatite-P and other immobile P forms but low in reactive P forms had the best burial efficiencies. At those sites, the material at the sediment surface had already lost most of its Fe-bound redox-sensitive P as well as easily degradable OP forms. In contrast, the burial efficiency of total P was lowest in the sediments rich in labile OP and/or Fe-bound P that strongly decreased with sediment depth. These types of sediments were found on the organic-rich eastern coast of the GoF where the lowest burial efficiency was 41%. This indicates that a relatively high proportion of P in the sediment surface in this area can be released from the sediment over time. However, it is noteworthy that this calculation assumes that the decrease in labile OP with sediment depth has mostly resulted from a slow degradation over the past 17–18 years. In other words, the contribution of the possible increase in sedimentation of OM (Jonsson & Carman 1994, Vaalgamaa & Conley 2008) is neglected. If the increased sedimentation of labile OP is mostly responsible for its observed vertical decrease, the burial efficiency values are underestimated. The burial efficiency values determined for the northeastern BS were close to those reported for other sea areas. Anschutz et al. (1998) suggest that in several continental margin sediments 70–80% of P in the sediment surface will be buried, while Sundby et al. (1992) estimated that about half of the deposited particulate P was buried in the Laurentian Trough (the Gulf of St. Lawrence). In contrast, burial efficiencies in the northeastern BS were higher than the burial efficiency calculated for the Aarhus Bay (Denmark) (close to 30%) on the basis of the burial and release of sediment P reported by Jensen et al. (1995).

The burial fluxes for P determined in the northeastern BS were probably influenced by the activity of benthic animals in oxic sediments. Bioturbation can enhance the burial of reactive P by mixing particles deeper into the sediment so that the P released from them during biogeochemical processes will be trapped in the sediment, and it can enhance the binding of P to Fe-oxyhydroxides by promoting oxidation. On the other hand, burrowing activity can increase the release of sediment P by enhancing microbial activity and by the upward transportation of pore water PO_4-P and sediment particles with sorbed P from deep, reduced sediment layers (Schink & Guinasso 1978, Holdren & Armstrong 1980, Aller 1988, Kristensen 1988, Andersen & Jensen 1991, Sundby & al. 1992, Slomp & al. 1998, Lewandowski & Hupfer 2005).

4.3.2 Potential for release of P from sediment reserves in the northeastern BS

Assuming that 1) all reactive P lost from the sediment since the year 1986 (observed as a decrease in reactive P with sediment depth) was released to the overlying water, 2) SAR has remained constant, and 3) the chemical composition of the material deposited remained more or less similar, a rough estimate of a long-term average value for the minimum annual P release from sediment P reserves can be calculated on the basis of P fractionation results and SAR values. It should be kept in mind, however, that all these assumptions are not fulfilled. SAR can vary, especially in estuaries and in shallow sea areas. It may also have increased in the GoF during the past decades because of increased production of OM as a result of eutrophication, as has been suggested, for example, for the Gotland Basin (Emeis & al. 2000) and for the shallow coastal bays in the northern GoF (Vaalgamaa & Conley 2008). In addition, alterations in O_2 conditions can induce drastic short-term changes in sediment P reserves in areas that have varying redox-conditions and high Fe-bound P in the surface layers. Nevertheless, the long-term average values for the minimum annual P efflux from the sediment varied from almost zero (0.04) to 7.9 mmol m^{-2} y^{-1}, corresponding to 1.3 to 244 kg km^{-2} y^{-1} within the whole study area (Table 3). Generally, these minimum P efflux values were highest in the estuaries, with an average value of 2.8 mmol m^{-2} y^{-1}. In the shallow coastal sediments in the AS and GoF it was 2.4 mmol m^{-2} y^{-1} (73.7 kg km^{-2} y^{-1}) and in the poorly oxygenated sediments of the open GoF (excluding the site in the northern BP) it was 0.6 mmol m^{-2} y^{-1} (18.9 kg km^{-2} y^{-1}). By comparison, utilising estimates of P loss from the sediment, Krom and Berner (1981) suggested that a minimum estimate of the mean annual flux of P in the Long Island Sound was about 4.0 to 7.7 mmol m^{-2} y^{-1} and Anschutz et al. (1998) found a flux of 7.5 mmol P m^{-2} y^{-1} in continental margin sediments.

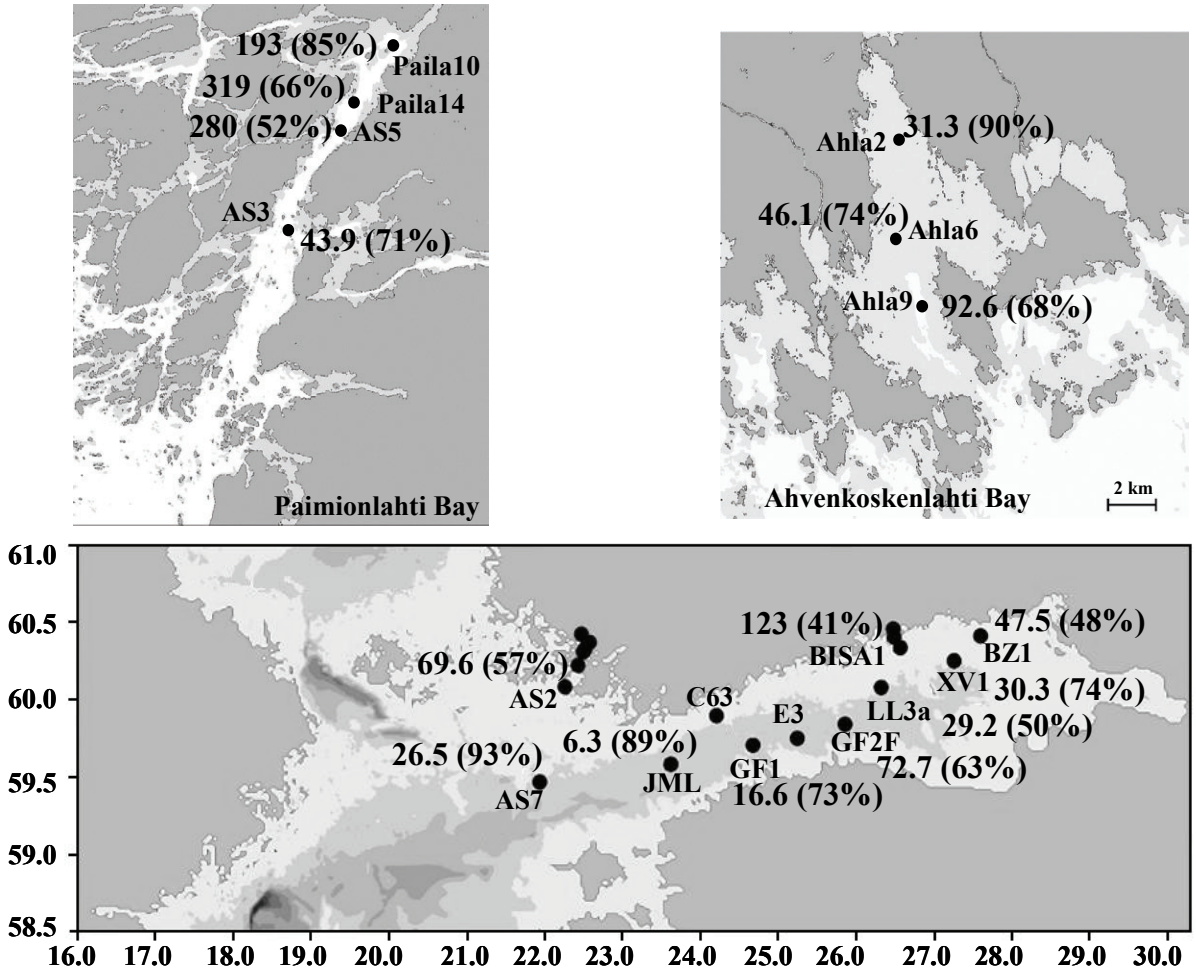


Fig. 8. Sedimentation of P (mmol m^{-2} y^{-1}) and burial efficiency (%) of sediment total P at the sampling sites (assuming constant SAR).

In this approach, the estimates probably have the highest uncertainties when applied to estuary sediments where the high SAR seemed to vary with time. Calculations based on the decrease in the reactive P with sediment depth during the past ca. 20 years suggest that, in the long term, the minimum estimate for P efflux in the organic-rich coastal sediments overlain by oxic near-bottom water would be higher than in the sediments of poorly oxygenated open sea areas. This differs from the commonly accepted view that the hypoxic areas contribute mostly to the release of P from sediment reserves. However, this outcome could simply be an overestimation of the long-term average for the minimum annual P release from the oxic organic-rich coastal areas as a result of omitting the possible increase in sedimentation of OM. On the other hand, the relatively stable vertical distribution of reactive P in the sediments of the poorly oxygenated areas in the western GoF and in the northern BP suggest that most of the redox-dependent and labile OP forms are already lost from the sediment. This means that the sediment P reserves are mainly in immobile forms. Thus, in these areas, the annual release of sediment P is probably dictated by mineralisation of freshly deposited OP. The mineralisation-derived P cannot be retained in the hypoxic surface sediments; therefore it is not included in the examined P reserves. At the (more or less) temporarily hypoxic sites, the redox-sensitive P, enriched in the surface layers, is prone to short-term release. According to Virtasalo et al. (2005) and Kotilainen et al. (2007), in the AS and on the northeastern coast of the GoF, the bottom sediments suffer from seasonal anoxia. The abundance of laminated sediments found in other areas in the BS, including the coastal areas (Jonsson & al. 1990, Jonsson & Jonsson 1988, Persson & Jonsson 2002), indicates an increased frequency of poor O_2 conditions during the past decades. It is possible that seasonal anoxia will become more frequent in coastal areas in the future due to climate change-induced increases in nutrient runoff (HELCOM

2007). In contrast, if O_2 conditions were to suddenly recover, for example, as result of artificial oxygenation of the bottom water, sorption of P forms bound to redox-sensitive Fe compounds at the sediment surface would be enhanced as long as the oxic conditions continued. A prerequisite for improved sorption ability is, however, that free sorption sites are available for P in the sediment.

The calculations for the long-term average values for minimum annual P release from the sediment P reserves could also suggest that, in addition to hypoxic open sea areas, the P release from sediment reserves may be important in the organic-rich oxic coastal areas in the long term. The release of sediment P in spite of oxic bottom water has been reported in several studies, and it is often connected to degradation of OM and formation of an anoxic zone at the sediment surface. Lee et al. (1977) suggested that, in the long term, especially in sediments of shallow lake areas, the slow but continuous release of P in aerobic conditions may be almost as high as that in anaerobic conditions. Holdren and Armstrong (1980), Boström et al. (1982), and Boström and Pettersson (1982) have also discussed release of P from lake sediments overlain by oxic near-bottom water. In addition, release of P in oxic conditions has been reported from estuarine sediments (Maher & DeVries 1994) and from marine sediments (Conley & al. 1997, Matthiesen & al. 1998).

In this study, the incubation-derived PO_4-P flux values (Table 1) varied greatly between the sites, as has been reported earlier for the GoF (Conley & al. 1997, Pitkänen & al. 2001). The highest values for incubation-derived PO_4-P fluxes were roughly one hundred times higher than the long-term average values for minimum P effluxes based on solid-phase P determinations. The peak value, 1774 μmol m^{-2} d^{-1} at the organic-rich eastern GoF (site XV1), was more than twice as high as the peak fluxes reported by Conley et al. (1997) and Pitkänen et al. (2001) in the GoF, but even higher values have been reported in organic-rich anoxic sediments (e.g., in the Cape Lookout Bight, USA; Klump & Martens 1981). However, the P releases determined by these two methods are not comparable because the incubation-derived PO_4-P flux represents a temporary situation (Krom & Berner 1981) and it does not take into account annual variation. In fact, at some sites, the incubation-derived PO_4-P flux was negative, demonstrating binding of P in the sediment instead of release. To include this type variation in the estimations, the measurements should be repeated many times during different seasons at each of the sampling sites, preferentially *in situ*. In addition, the function of the sediment as a source and sink for P and the dynamic relationships between solid and solution P could be studied by means of more sensitive methods, for example desorption-sorption graphs (e.g. Froelich 1988, Slomp & al. 1998, Koski-Vähälä & Hartikainen 2000, 2001). This approach could also be useful when estimating the effect of decreases in water column PO_4-P concentrations (e.g., as result of reduced P loading) on sediment P reserves. Theoretically, in these conditions, the reserves of reactive P in the sediment will slowly diminish with time, because the deposition of particulate P decreases. Accordingly, with time, the degree of P saturation of the sorption components will gradually decrease. This means that in oxic conditions a lower P concentration in the near-bottom water can be maintained without enhanced P flux from the sediment. However, further studies on P exchange between the sediment and near-bottom water in the BS are needed to better understand these processes.

The long-term average for the sediment P release represents an average result, reflecting the fate of sediment P transformed by various biogeochemical processes over time, and in varying conditions. In addition, it represents a minimum estimate only (Krom & Berner 1981) and it does not show the short-term changes caused, for example, by degradation of newly deposited algal material, which can temporarily cause a significant peak in sediment P release (Krom & Berner 1981, Garber 1984, Andersen & Jensen 1992, Enoksson 1993, Conley & Johnstone 1995). Enhanced release of P from deposited algal material may last a few days or a few weeks, especially if the degradation processes consume most of the O_2 from the sediment-water interface (Andersen & Jensen 1992, Conley & Johnstone 1995). Despite temporarily pronounced P release after settling of algal blooms, some sediments may act as a sink for P for most of the year (e.g. Klump & Martens 1987, Kamp-Nielsen 1992). In addition, in the present study, the P efflux based on fractionation of solid phase P and SAR (determined from ^{137}Cs peak values) averages the P release or binding during the 17–18 year period after 1986. This means that the approach probably underestimates the P efflux during the recent years, which were characterised by bad O_2 conditions and, at the same time, possibly overestimates P efflux during years when O_2 conditions were good. According to the monitoring data from FIMR, O_2 conditions in the GoF deteriorated in the late 1990s, which was reflected in elevated PO_4-P concentrations in the water (Olsonen 2007, Fleming-Lehtinen & al. 2008).

The above discussion stresses the difficulties in assessing P release from bottom sediments in the BS. For example, it has been estimated that the internal P loading in the GoF is about 4 000–18 000 t y^{-1} (Pitkänen & Kiirikki 2005). This study reveals that examining the quantity of both immobile and reactive P reserves in the sediments and their changes over time in different sea areas offers a tool for improving the estimates of internal P loading, although there are some uncertainties and limitation

as presented above. For example, if we suppose that all of the shallow (<60 m) and deep (>60 m) areas in the GoF have similar chemical compositions and similar long-term averages for minimum annual release of sediment P, as the coastal and open sea areas examined in this study, we can very roughly estimate an average value for minimum annual release of sediment P for the whole GoF. Approximating that about 83% of the ca. 29 600 km^2 surface area of the GoF is shallower than 60 m and 17% is deeper (Pekka Alenius, FIMR, pers. com.), the long-term average for minimum annual P release from sediment P reserves would be slightly over 1900 t P y^{-1}. The changes in sediment P reserves over time can be used in estimating P release from bottom sediments of the BS, but additional information is needed. 1) Short-term P release caused by degradation of newly deposited algal material in each area should be determined by frequent sampling. 2) The present study showed that there is considerable spatial variation in the chemical composition of sediment P, thus, more comprehensive spatial characterisation of chemical composition should be undertaken. 3) Different bottom types should be investigated. In the present study, most of the sampling sites represented soft sediments that only cover approximately one third of the surface area (Vallius 1999a). The chemistry of P and its release from the different bottom types in the BS is still poorly described. 4) The possible increase in the SAR should be taken into account. 5) Better estimates of the degradability of sediment OP are needed. OP proved to constitute a considerable part of sediment P reserves in the organic-rich sediments of the GoF, but its chemical composition remained unclear. The composition of OP could be characterised by, for instance, ^{31}P-NMR-techniques.

5. CONCLUSIONS

Considering eutrophication, it is important to characterise sediment P reserves in order to be able to evaluate what portion will be buried and removed from the nutrient cycle, and what portion may serve as source of P for the overlaying water over time. Furthermore, comparison of the chemical character of sediment P in different sea areas gives valuable information on which areas are the most susceptible to P release from sediment reserves and which areas rather act as sinks for P and bury most of the P in the sediment.

The fractionation scheme and sampling and storing practices used in this study showed reproducible results and reliable characterisation of six different binding or solubility forms of sediment P in the oxic and hypoxic northeastern BS sediments that are rich in organic matter and iron and poor in $CaCO_3$. However, when working with fresh sediments, especially with the reduced sediments that are common in the BS, the samples should be protected from atmospheric oxygen during sampling, storage and also during the initial stages of extraction. When protected from oxygen, the reduced sediment samples experienced only minor changes and only after a few months of storage. In contrast, if the reduced sediment was allowed to react with oxygen, clear changes in the P chemistry were detected, especially in the redox-sensitive and soluble forms.

The chemical characterisation of sediment P by separating it into six different binding and solubility forms revealed marked spatial differences in the composition of sediment P reserves in the AS and GoF, northeastern BS. In two shallow estuaries, the sediments were characterised by high concentrations of P bound to hydrated oxides of iron and aluminum. Generally, iron-bound P was abundant in the surface sediments in the areas where the redox-conditions allowed the formation of ferric-oxyhydroxides. The concentration of iron-bound P sharply decreased below the surface layer because of the reduction-induced dissolution of iron and consequent release of iron-bound P. However, in the deep layers in the estuarine sediments, iron compounds, part of which remained in ferric form, probably because of the high sedimentation rate and incomplete reduction, buried part of the river-transported P, preventing its transportation to coastal sea areas. Aluminum-bound P, which was abundant in the estuary sediments high in eroded clayey material, was one of the most stable P forms in the sediments. This is important with respect to binding and burial of P, because aluminum oxides are not sensitive to changes in redox potential and, unlike iron oxides, also retain P in reduced conditions.

The areas that were most affected by transportation of fine particulate material, the inner estuaries or shallow coastal areas, were enriched in calcium-bound and apatite-P. This relatively stable P form was also abundant in the western open GoF and in the northern BP where the sediment material had lost most of its reactive P forms. Accordingly, the burial efficiency of total P in the sediment surface layer was highest in these areas. On the other hand, apatite-P and organic P differed in their spatial distribution: apatite-P decreased eastwards in the GoF while organic P increased. Refractory organic P and especially labile organic P increased eastwards, towards the inner Gulf, following the increasing concentration of organic carbon. Part of the organic P was buried and removed from the nutrient cycle, but part of it was degraded in the sediment over time. The large reserves of organic P, particularly in the eastern GoF, seem to constitute an important source of P in the long term. Assuming the sedimentation to be constant, the burial efficiency of P in the sedi-

ment surface was lowest in the organic-rich sediments in the eastern GoF. In oxic conditions, ferric-oxyhydroxides in the surface sediment will retain the mineralisation- or reduction-released P diffusing upwards in the sediment pore-water. However, the abundance of organic matter and seasonal stratification in the shallow sub-basins can result in reducing conditions at the sediment surface and, consequently, in the release of Fe-bound P.

The sediment properties were reflected in the chemistry of the near-bottom water and sediment pore water, and the dissolved species indicated variable redox conditions in the study area. Because of the short-term changes in the redox conditions and the spatial heterogeneity caused by variable bottom topography and differences in sediment accumulation, the fate of sediment P can vary within a relatively small area. The chemical composition of sediment P dictated its behaviour and responses to the changing environmental conditions at the sediment-water interface. In addition, chemical differences in the P reserves affect the spatial variation in the burial of sediment P. Thus, the fractionation analysis is a useful tool to characterise sediment P reserves and it produces valuable information on the fate of sediment P transformed in various biogeochemical processes over time, and on the potential of sediment P reserves to release P.

The implication of this research is that, when evaluating the release of sediment P to the overlaying water and the contribution of sediment P reserves to eutrophication, it is important to take into account the chemical character of the sediment P. Furthermore, the considerable spatial variation in the chemical forms of P found in this research area emphasises the importance of characterisation of the sediment P reserves in other areas of the BS as well, in order to improve our understanding of the role of sediment P in eutrophication of the BS.

Acknowledgements

Many people have helped me with various steps in the making this thesis and I want to express my gratitude to at least some of them here. First, I want to thank my supervisors, Helinä Hartikainen for familiarising me with the chemistry of phosphorus, for giving scientific advice for my PhD, and for helpful and constructive comments on all the manuscripts, and Mirja Leivuori, for organizing our research cruises and facilities in the lab. I acknowledge the pre-examiners, Caroline Slomp and Daniel Conley, whose professional advice and comments helped to improve the manuscript of this thesis. I also want to thank Alf Norkko, Joanna Norkko, and Aarno Kotilainen for valuable comments on the thesis and encouragement during the final steps of my PhD work. I also thank Per Jonsson for agreeing to be opponent for the public defence of my doctoral thesis.

My warmest thanks go to Tanja Kinnunen for her invaluable help in the lab with P fractionations, her positive attitude, and all her support over the years while struggling with the numerous sediment samples. I also want to thank Kirsi Hyvärinen and Pia Varmanen for phosphorus analyses and other help in the lab, Jere Riikonen for metal analyses, and all of them for help in sampling during our research cruises. I'm grateful to the other technical personnel of FIMR, especially Jussi Rapo, Henry Söderman and Pekka Kosloff, who did the sediment sampling on the R/V Aranda and helped to solve many technical problems. I wish also to thank the crew of the great research vessel of FIMR, the R/V Aranda; I have always enjoyed working onboard.

I want to thank Finnish marine geologists for excellent cooperation and cheerful company during sampling cruises, especially Aarno Kotilainen and Henry Vallius, who have taught me a lot about Baltic Sea sediments. I'm indebted to Hannu Haahti for P-flux determinations and Kalervo Mäkelä for determining nutrients at the sediment-water interface. I also want to thank Henning Jensen for advice with the phosphorus fractionation method and Ville Hallikainen for help and advice with statistical analysis. Thanks belong also to our new research group of benthic processes at FIMR, led by Alf Norkko, for being an inspiring and fun team. I also thank Christina Lyra and Hanna Sinkko for help with SPSS and for great cooperation and stimulating discussions on what is going on in the marine sediments.

I wish to thank the always helpful personnel of the library of FIMR, Helena Huttunen, Anne Martikainen, and Leena Parkkonen, for finding me the numerous scientific articles and books from all around the world. I also thank Ritva Eloranta for helping me with numerous practical things during the years. I wish to thank Leena Roine and Leena Parkkonen for editing this thesis and Kathleen Ahonen and Mary Metzler for language revision of the manuscripts.

I want to express my gratitude to the heads of the departments I have been employed to at FIMR, Matti Perttilä (the former Department of Chemical Oceanography) and Markku Viitasalo (Baltic Sea Processes), for giving me the opportunity to work with marine sciences. I'm also grateful for Liisa Autio who gave me the idea for applying to FIMR in the first place and, with Helinä Hartikainen, originally suggested chemistry of phosphorus in marine sediments to be the subject for my PhD thesis.

I'm deeply grateful to FIMR, The Academy of Finland and Ministry of Environment, The Kone Foundation, and The Maj and Tor Nessling Foundation for funding this research. The work was carried out at FIMR, mainly in a research project that included to the SEGUE research consortium and was a

part of the Baltic Sea Research Programme (BIREME) by Academy of Finland.

Most of all I'm grateful to my dear family: my parents Maija and Heikki, for supporting and encouraging me in my studies and in all other steps of my life, and my siblings Marianna, Matti, and Pertti, for always taking care of your little sister, supporting, listening, and making my life easier in many ways. I want to thank all my friends, at work and in private life, who have made the long working days fun, and the free time even more fun. I want to thank especially my dear friends Helena and Sanna for your friendship during all the years; for listening, encouraging, and sharing countless conversations on all kinds of topics, including the experience (and trouble) of making a PhD. Your company always cheers me up.

Finally, I want to express my gratitude to the chief director of FIMR, Eeva-Liisa Poutanen, for her supportive leadership, standing up for Finnish marine research, and for creating a wonderful team spirit. I also want to thank all the personnel of FIMR who made the institute such a great, memorable, and unique place of work. Present plans to close down the creditable 90-year old institute are regrettable. I feel privileged that I had the opportunity to work and make my PhD at FIMR.

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APPENDIX

Table 4a–f. Elemental composition of fractionation extracts at each site. Concentrations are presented in μmol g^{-1} DW.

		NaCl						NaBD						NaOH						HCl (0.5 M)						HCl (1 M)					
Site	cm	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe
Pail10	1	-	1.7	0	33.7	1.2	0	-	4.6	0.8	4.3	1.9	129	-	303	173	0	0.1	14.5	-	97.6	137	14.6	1.6	155	-	-	-	-	-	-
	2	-	1.7	0	32.1	0.6	0	-	5.4	1.0	5.4	1.8	106	-	340	211	0.7	0.4	48.4	-	103	145	14.6	1.7	182	-	-	-	-	-	-
	3	85.9	2.1	0.2	31.4	0.4	0.1	8.3	5.4	0.4	5.5	1.4	32.2	0.5	278	159	0	0	2.2	51.7	113	154	16.5	2.0	244	-	-	-	-	-	-
	4	84.2	2.5	0.4	31.1	0.3	0.2	7.8	5.7	0.6	5.2	1.1	24.2	1.6	277	159	0	0	4.6	50.9	113	151	15.5	1.9	246	-	-	-	-	-	-
	5	82.6	2.4	0.3	31.1	0.3	0.1	6.5	5.7	0.5	4.4	0.9	36.1	2.1	275	165	0	0	6.0	50.4	109	145	14.9	1.6	218	-	-	-	-	-	-
	6	81.4	2.4	0.3	32.3	0.3	0.1	6.1	5.9	0.7	4.6	0.9	57.6	2.3	271	167	0.1	0	6.2	51.7	111	148	15.4	1.6	205	-	-	-	-	-	-
	7	79.2	2.4	0.3	30.2	0.2	0.2	7.1	5.8	0.9	5.1	0.8	64.8	1.7	269	170	0	0	5.2	51.0	107	146	15.2	1.6	199	-	-	-	-	-	-
	8	79.7	2.2	0.2	30.7	0.2	0.1	6.6	7.0	0.9	4.7	0.8	44.1	0.7	279	150	6.8	0	2.0	45.9	100	159	13.3	1.7	182	-	-	-	-	-	-
	9	78.4	2.4	0.4	32.2	0.2	0.2	6.6	6.5	0.9	5.5	0.7	43.0	0.2	296	189	0.2	0.1	16.1	46.0	99	150	14.6	1.7	187	-	-	-	-	-	-
	10	77.7	2.1	0.2	30.4	0.2	0.1	5.9	6.5	1.2	4.2	0.7	39.5	0.4	272	170	0.4	0	2.1	45.2	99	176	13.4	1.9	175	-	-	-	-	-	-
	15	81.5	2.4	0.4	32.5	0.2	0.2	9.1	10.4	1.7	7.4	0.9	36.5	3.1	294	161	0	0	8.4	49.5	109	142	14.8	1.4	197	-	-	-	-	-	-
	20	87.9	2.4	0.3	35.6	0.3	0.2	6.6	8.2	0.8	5.0	1.1	29.7	3.1	291	164	0	0	8.4	48.3	109	140	14.1	1.4	203	-	-	-	-	-	-
	25	91.5	3.0	0.3	43.3	1.2	1.2	2.9	9.5	1.4	2.7	0.6	50.6	5.1	303	173	0	0.1	11.8	50.9	118	151	15.0	1.2	197	-	-	-	-	-	-
Pail14	1	-	2.4	0	39.3	2.5	0	-	6.8	1.5	5.8	3.2	152	-	325	110	0	0	1.2	-	105	126	16.0	1.6	151	-	-	-	-	-	-
	2	-	2.8	0	39.0	1.3	0	-	11.6	3.1	9.9	5.5	84.5	-	429	127	0	0.1	7.5	-	133	177	21.4	2.4	300	-	-	-	-	-	-
	3	-	3.7	0.1	35.5	1.9	0.2	-	17.9	7.8	4.8	3.1	56.6	19.1	386	157	0.3	0.3	37.2	59.7	126	154	19.1	2.0	211	-	-	-	-	-	-
	4	-	3.2	0.1	33.8	3.4	2.6	-	17.4	8.7	2.6	2.0	79.0	14.1	369	160	0.3	0.2	27.1	60.4	128	154	17.1	1.8	167	-	-	-	-	-	-
	5	-	3.0	0	32.3	1.7	0.2	-	5.9	1.2	3.7	2.7	61.1	3.8	340	140	0	0.1	9.0	58.8	125	152	16.8	1.9	185	-	-	-	-	-	-
	6	-	3.6	0.1	34.3	2.6	2.5	-	6.7	1.2	3.3	1.8	81.5	0	326	129	0	0	1.6	59.9	131	157	17.2	1.8	193	-	-	-	-	-	-
	7	-	3.7	0.1	35.9	2.4	3.7	-	8.1	1.2	3.4	1.6	55.0	1.4	339	134	0	0	4.0	57.5	130	155	16.9	1.7	227	-	-	-	-	-	-
	8	-	3.5	0	35.7	2.3	2.7	-	7.8	1.2	3.1	1.2	57.5	2.8	327	134	0	0	6.6	55.7	124	147	15.6	1.5	196	-	-	-	-	-	-
	9	74.6	2.5	0.2	29.8	1.0	0.1	5.6	6.9	0.6	4.5	2.0	16.8	4.5	324	135	0	0.1	10.0	54.1	119	155	17.2	2.2	240	-	-	-	-	-	-
	10	78.2	2.6	0.1	34.0	0.9	0.1	6.2	7.7	0.7	4.9	2.2	17.9	5.7	331	136	0.2	0.1	12.9	53.7	121	156	17.8	2.3	255	-	-	-	-	-	-
	15	83.7	3.1	0.3	35.4	0.4	0.2	6.9	8.8	0.5	5.2	1.9	27.0	4.5	356	126	0	0.1	11.2	52.9	125	150	17.7	1.9	210	-	-	-	-	-	-
	20	89.8	3.2	0.2	37.3	1.7	0.6	3.5	7.9	0.9	3.2	1.5	36.0	6.2	405	140	0	0.1	15.0	53.8	126	150	17.3	1.9	217	-	-	-	-	-	-
	25	99.3	3.0	0.3	48.8	1.3	0.3	4.4	7.3	0.7	4.7	1.6	30.5	6.5	431	150	0	0.1	15.7	52.2	125	149	16.2	1.5	201	-	-	-	-	-	-
ASS	1	-	2.6	0	37.8	3.0	0	-	6.0	0.8	5.4	3.7	78.8	-	325	104	0	0.1	8.1	-	104	132	17.5	1.9	242	-	-	-	-	-	-
	2	-	3.4	0	39.0	2.0	0.4	-	7.1	1.0	5.6	4.8	56.6	-	365	112	0	0	1.2	-	118	155	19.9	2.7	290	-	-	-	-	-	-
	3	95.7	4.4	0.5	35.1	0.9	0.4	6.8	7.1	1.0	5.2	3.3	24.9	0.2	318	110	0	0	2.1	63.5	134	161	19.2	2.5	231	-	-	-	-	-	-
	4	91.2	3.6	0.6	34.0	1.4	0.3	5.4	6.8	1.6	5.6	2.1	22.1	0.3	324	120	0	0	2.2	61.1	130	156	23.6	2.0	182	-	-	-	-	-	-
	5	96.3	4.2	0.4	33.2	1.1	0.3	6.4	7.0	1.5	4.5	2.3	23.9	0.2	338	120	0	0	2.2	59.7	128	154	18.5	2.0	201	-	-	-	-	-	-
	6	83.3	3.9	0.4	30.4	1.3	0.3	11.1	12.3	5.3	5.4	3.0	32.8	0.3	328	119	0.2	0	2.3	61.2	133	159	17.9	2.2	215	-	-	-	-	-	-
	7	86.5	3.4	0.2	31.8	1.5	0.5	6.7	6.2	1.3	4.2	2.2	25.5	0.1	345	120	0	0	1.7	53.4	117	147	18.4	1.9	216	-	-	-	-	-	-
	8	81.6	2.9	0.2	32.5	1.9	0.6	5.3	7.3	1.4	3.9	2.1	25.2	0.2	352	120	0	0	1.9	53.7	123	152	17.7	1.8	242	-	-	-	-	-	-
	9	84.4	3.4	0.2	34.4	2.2	0.6	4.5	10.4	3.8	3.4	1.5	25.7	1.8	345	125	0	0	5.9	54.3	122	150	17.9	1.7	214	-	-	-	-	-	-
	10	80.3	3.0	0.1	30.0	1.1	0.1	7.2	7.0	1.2	4.1	3.0	24.1	0.7	351	130	0	0	3.4	54.5	122	151	18.9	2.3	239	-	-	-	-	-	-
	15	83.8	3.0	0.2	34.6	0.8	0.1	6.3	10.9	1.1	5.4	2.0	26.1	3.5	403	128	0	0.1	9.7	56.8	132	155	18.9	1.9	225	-	-	-	-	-	-
	20	83.5	2.9	0.2	35.7	0.3	0.1	9.3	9.4	0.4	6.5	2.2	27.0	4.5	410	125	0	0.1	11.8	56.2	130	152	18.0	2.0	211	-	-	-	-	-	-
	25	85.4	3.1	0.3	36.1	0.3	0.2	8.1	8.7	0.8	6.1	1.6	19.5	5.9	433	136	0	0.1	14.0	57.0	126	152	18.2	1.6	162	-	-	-	-	-	-

Table 4b.

Site	cm	NaCl						NaBD						NaOH						HCl (0.5 M)						HCl (1 M)					
		Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe
AS3	1	-	2.2	0	39.6	0.6	0	-	7.5	1.1	4.2	2.2	146	-	362	122	0.9	0.4	34.0	-	97.8	115	20.4	1.2	104	-	-	-	-	-	-
	2	-	2.6	0	35.5	0.7	0	-	11.0	3.8	5.8	1.4	113	-	391	115	0.5	0.2	21.6	-	103	127	22.9	1.4	124	-	-	-	-	-	-
	3	86.3	3.2	0.4	35.3	0.7	0.2	3.1	7.1	0.3	3.8	0.7	17.7	0.3	328	88.7	0	0	1.4	60.2	107	153	22.0	1.6	181	-	-	-	-	-	-
	4	77.4	3.0	0.4	31.4	0.4	0.2	4.4	6.3	0.4	4.9	0.7	18.5	0.3	334	87.4	0	0	1.4	54.9	104	140	21.3	1.4	151	-	-	-	-	-	-
	5	77.1	3.2	0.3	32.8	0.6	0.2	2.8	6.7	0.4	3.6	0.6	19.2	0	340	90.0	0	0	1.4	56.8	113	142	21.6	1.4	150	-	-	-	-	-	-
	6	77.0	3.1	0.4	35.3	0.6	0.2	2.8	6.4	0.2	3.9	0.6	20.6	0.2	341	87.5	0	0	1.5	56.7	112	144	21.6	1.4	148	-	-	-	-	-	-
	7	76.2	2.7	0.2	41.2	0.5	0.1	3.1	6.7	0.3	4.7	0.7	24.6	0.4	364	91.6	0	0	2.3	56.4	111	146	21.7	1.5	165	-	-	-	-	-	-
	8	82.7	3.0	0.4	36.0	0.6	0.2	3.0	7.1	1.0	4.6	0.7	25.1	0.5	380	99.4	0	0	3.1	52.9	116	140	22.5	1.3	162	-	-	-	-	-	-
	9	80.6	3.0	0.3	36.9	0.4	0.1	4.0	7.6	1.3	5.4	0.7	25.9	0.3	373	96.4	0	0	2.6	52.3	115	136	22.0	1.3	166	-	-	-	-	-	-
	10	83.3	3.2	0.2	39.2	0.8	0.1	2.8	7.8	1.1	4.1	0.8	26.7	0.1	372	95.5	0	0	2.3	54.5	121	142	21.9	1.4	174	-	-	-	-	-	-
	15	81.6	2.6	0.2	37.6	0.6	0.1	4.8	9.2	1.0	5.6	1.6	21.6	3.7	368	105	0.1	0.1	10.8	55.3	126	150	22.9	1.6	194	-	-	-	-	-	-
	20	85.1	2.3	0	37.8	0.8	0	5.2	8.5	0.4	6.1	1.6	13.4	3.1	173	91.8	0	0.1	7.5	46.9	104	132	21.9	1.5	155	-	-	-	-	-	-
	25	82.6	2.8	0	35.2	0.6	0	7.6	7.5	0.3	6.6	2.2	13.3	0.7	133	78.3	0.1	0	1.6	54.5	115	147	23.4	1.7	153	-	-	-	-	-	-
Ahal2	1	74.3	2.5	0	45.7	2.0	0.2	2.0	3.9	2.2	2.0	1.5	69.8	0.5	358	104	0	0	3.3	33.4	80.1	91.2	22.3	1.0	89.0	-	-	-	-	-	-
	2	70.3	2.4	0	44.8	1.7	0.1	1.8	4.2	2.3	0.8	0.8	72.5	0	387	109	0	0	3.5	36.0	85.8	95.6	22.4	1.0	87.1	-	-	-	-	-	-
	3	71.0	3.4	0	42.1	1.7	0.4	1.6	3.8	1.8	1.0	0.6	61.4	0	381	110	0	0	3.5	35.5	84.8	95.1	22.0	1.0	94.4	-	-	-	-	-	-
	5	67.9	2.7	0	38.3	1.6	0.4	1.5	4.1	1.9	0.7	0.4	38.1	0	372	106	0	0	3.1	34.6	84.2	93.6	21.7	0.9	106	-	-	-	-	-	-
	7	69.6	2.7	0	37.8	1.4	0.3	2.0	4.0	2.0	1.2	0.4	11.7	0.3	365	105	0	0	3.7	34.2	85.2	94.5	22.4	0.9	121	-	-	-	-	-	-
	10	79.4	2.8	0	40.9	0.6	0.2	2.4	3.1	1.3	1.7	0.6	9.8	0	335	98.4	0	0	3.1	35.4	86.8	98.5	24.4	1.1	105	-	-	-	-	-	-
	15	75.1	2.9	0	38.0	0.6	0.1	2.5	2.9	1.4	1.7	0.5	4.9	0	288	109	0	0	2.7	34.6	85.7	99.1	22.2	1.2	114	-	-	-	-	-	-
	25	80.1	3.8	0	37.2	0.5	0	3.2	3.6	1.2	1.2	0.5	1.9	0	397	93.4	0.1	0	2.5	37.5	92.3	107	20.4	1.4	124	-	-	-	-	-	-
Ahla6	1	133	4.1	0	59.5	2.1	0.2	3.9	5.5	1.8	4.1	1.2	32.3	0	660	122	0.1	0	4.5	44.1	113	131	24.9	1.4	154	-	-	-	-	-	-
	2	104	3.7	0	49.8	1.6	0.1	3.6	5.9	2.0	2.2	1.0	28.7	0	649	122	0	0	3.3	41.8	107	122	20.1	1.3	143	-	-	-	-	-	-
	3	108	4.2	0	50.2	1.8	0.3	4.5	6.9	2.2	2.6	1.3	24.7	1.0	662	124	0	0	7.0	45.2	117	133	21.7	1.5	159	-	-	-	-	-	-
	5	112	4.3	0	51.0	1.6	0.3	4.2	5.5	1.5	2.8	1.0	18.1	0	690	120	0	0	3.5	42.6	113	131	20.9	1.4	150	-	-	-	-	-	-
	7	107	3.5	0	47.1	1.6	0.3	4.0	5.4	1.6	2.9	0.9	15.7	0	731	121	0	0	4.2	41.5	111	124	19.4	1.4	144	-	-	-	-	-	-
	10	109	4.1	0	48.3	2.1	0.1	4.1	5.2	1.4	3.0	1.4	15.2	0	699	124	0	0.1	4.1	41.5	109	121	19.3	1.7	133	-	-	-	-	-	-
	15	115	5.0	0	51.9	2.6	0.1	6.6	21.1	7.8	5.0	2.3	19.0	0	675	125	0.2	0.1	3.9	44.7	117	135	21.0	2.2	146	-	-	-	-	-	-
	25	108	4.5	0	48.0	3.2	0	4.9	6.5	1.1	4.4	2.9	25.0	0	645	119	0	0.1	3.6	45.9	119	139	18.8	2.7	181	-	-	-	-	-	-
Ahla9	1	128	5.1	0.7	48.3	2.3	0.5	7.0	5.6	1.5	6.9	3.3	44.8	2.2	687	109	0.5	0	10.6	26.5	64.2	73.5	11.6	1.1	84.4	-	-	-	-	-	-
	2	151	8.4	0	66.9	3.5	2.6	11.6	10.1	2.5	5.0	5.4	64.1	0	1038	156	0	0	3.8	48.1	122	136	20.1	2.1	181	-	-	-	-	-	-
	3	109	5.0	0.5	46.9	1.3	0.4	13.9	8.0	2.1	11.4	4.6	39.7	0	795	112	0.4	0	5.5	35.0	94.9	113	18.9	2.4	136	-	-	-	-	-	-
	5	125	6.1	0.4	50.5	1.3	0.2	16.2	10.0	1.7	12.2	5.8	51.3	0.1	959	122	0.2	0	4.6	39.4	106	134	21.1	2.0	155	-	-	-	-	-	-
	7	124	6.1	0.8	49.9	1.7	0.4	11.2	8.8	1.8	10.3	4.6	32.9	0	685	99.1	0	0	3.1	42.2	115	139	21.7	2.2	170	-	-	-	-	-	-
	10	120	6.4	0.4	49.3	1.2	0.2	10.2	9.1	1.6	9.2	3.4	36.6	0.9	939	130	0.4	0	8.3	42.4	121	137	20.4	1.9	179	-	-	-	-	-	-
	15	113	5.9	0.5	48.6	1.7	0.2	7.6	8.9	2.2	8.5	3.1	27.8	9.5	962	159	1.6	0.4	30.2	39.3	99.9	119	18.1	1.5	107	-	-	-	-	-	-
	25	106	4.7	0.3	47.1	2.4	0.1	7.1	9.8	2.1	9.3	4.3	36.9	7.8	938	160	1.3	0.3	28.6	38.8	105	126	17.8	1.9	157	-	-	-	-	-	-

Table 4c.

Site	cm	NaCl						NaBD						NaOH						HCl (0.5 M)						HCl (1 M)					
		Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe
AS7	1	105	6.9	0.3	29.6	0.3	0.2	3.9	8.0	2.0	1.9	0.6	21.2	1.0	328	33.7	0.1	0	3.3	46.0	93.1	94.2	29.1	1.1	128	-	-	-	-	-	-
	2	90.9	7.9	0.6	27.3	0.4	0.5	3.4	6.5	2.0	2.1	0.7	16.2	0.8	380	38.7	0	0.1	3.3	45.3	99.7	100	27.4	1.2	107	-	-	-	-	-	-
	3	107	9.9	0.8	31.2	0.5	0.6	3.3	5.0	1.3	1.9	0.8	11.0	0.9	445	40.7	0	0.1	3.5	48.0	109	110	29.4	1.3	103	-	-	-	-	-	-
	4	77.3	5.7	0.4	26.8	0.4	0.2	2.9	6.1	0.7	2.0	0.8	7.6	0	353	41.4	0	0	2.3	53.1	98.8	123	26.3	1.6	110	-	-	-	-	-	-
	5	83.6	3.3	0.4	30.1	0.9	0.2	2.1	6.8	0.6	1.7	0.5	10.4	0.2	399	46.8	0	0	3.0	54.7	102	127	25.3	1.5	131	-	-	-	-	-	-
	6	78.4	5.2	0.3	27.1	0.4	0.2	3.9	7.0	0.7	1.9	1.0	8.1	0.1	397	44.5	0	0	2.4	52.9	97.1	122	28.2	1.7	118	-	-	-	-	-	-
	7	72.5	4.8	0.3	25.6	0.4	0.1	3.1	5.9	0.7	2.2	0.8	7.4	0	386	42.5	0	0	2.2	50.5	93.7	116	27.4	1.7	110	-	-	-	-	-	-
	8	70.4	4.9	0.2	25.8	0.4	0.1	3.5	5.8	0.6	1.8	0.9	7.2	0	350	40.6	0	0	2.2	48.2	97.1	113	28.5	1.7	105	-	-	-	-	-	-
	9	82.6	3.4	0	29.8	1.0	0	1.9	7.0	0.9	1.8	0.6	11.5	0.4	429	44.5	0	0.1	3.8	48.9	119	114	29.7	1.5	114	-	-	-	-	-	-
	10	76.6	7.7	0.5	26.3	0.2	0.3	3.2	6.0	0.7	2.4	0.9	5.3	0.4	419	42.9	0	0.1	3.5	45.8	109	107	29.0	1.5	98.5	-	-	-	-	-	-
	15	75.0	7.5	1.2	27.4	0	0.6	3.7	4.4	0.4	2.6	0.9	2.6	0.4	223	35.0	0	0.1	1.7	46.3	110	110	29.0	1.8	106	-	-	-	-	-	-
	20	64.3	4.8	0	23.9	0	0	3.6	5.3	0.5	2.3	0.8	1.3	0.5	193	35.7	0	0.1	1.5	48.4	109	113	29.7	1.6	93.6	-	-	-	-	-	-
	25	57.8	4.1	0	20.7	0.1	0	4.0	5.2	0.2	2.2	0.5	2.0	0.5	161	34.0	0	0	1.4	43.2	95.1	97.4	29.0	1.6	100	-	-	-	-	-	-
JML	1	191	9.1	0	61.6	2.1	0	4.1	6.8	0.8	3.4	1.0	18.9	0.9	314	23.9	1.6	0	4.3	56.8	53.9	50.5	48.1	0.9	71.1	-	-	-	-	-	-
	2	167	7.9	0	49.8	0.5	0	6.8	6.8	0.9	4.7	0.7	13.7	1.0	516	44.3	0.8	0.2	5.5	58.6	89.8	91.5	44.6	1.4	105	-	-	-	-	-	-
	3	128	7.0	0	39.4	0.2	0	5.0	6.5	0.8	3.8	0.8	8.4	0.7	614	44.0	0	0.1	4.3	40.5	93.4	92.0	25.8	1.3	89.7	-	-	-	-	-	-
	4	110	4.3	0	35.8	0.1	0	3.2	6.1	0.7	2.8	1.3	11.5	0.7	553	55.1	0	0.1	4.4	42.7	103	101	26.2	1.4	97.9	-	-	-	-	-	-
	5	106	3.8	0	36.4	1.3	0	1.7	6.8	0.5	2.5	0.6	17.1	1.0	584	58.9	0.1	0.1	5.6	41.7	102	100	25.0	1.4	101	-	-	-	-	-	-
	6	113	5.0	0.7	39.8	1.2	0.6	3.3	8.7	1.5	3.6	0.9	21.1	1.7	546	53.3	0	0.2	5.2	42.5	108	108	28.0	1.6	105	-	-	-	-	-	-
	7	108	7.6	1.0	36.9	0.5	0.8	5.2	8.1	1.4	4.6	1.2	10.3	1.1	529	50.7	0	0.1	3.9	43.7	107	107	30.3	1.8	107	-	-	-	-	-	-
	8	103	5.8	1.1	36.0	0.4	0.9	4.4	8.2	1.8	4.0	1.3	9.5	1.2	524	50.9	0	0.2	4.3	40.2	102	102	28.1	1.7	109	-	-	-	-	-	-
	9	95.1	3.7	0.3	34.4	1.3	0.3	3.0	7.2	1.4	3.2	0.6	12.0	0.9	475	49.9	0	0.1	3.6	39.1	101	102	27.9	1.8	124	-	-	-	-	-	-
	10	90.6	3.4	0.2	34.8	1.7	0.3	2.3	7.0	0.8	3.2	0.5	17.3	1.2	506	52.3	0	0.1	4.2	49.0	121	121	26.5	1.7	135	-	-	-	-	-	-
	15	77.7	3.5	0	28.5	0	0.1	4.8	6.1	0.5	4.3	1.7	3.0	0.5	181	37.5	0	0.1	1.6	41.9	90.4	97.9	26.9	1.6	87.5	-	-	-	-	-	-
	20	73.9	2.1	0	30.2	0.7	0	4.2	6.9	0.3	4.8	1.0	7.3	0.1	167	33.0	0	0	1.5	62.5	87.4	95.5	52.1	2.0	127	-	-	-	-	-	-
	25	88.5	2.2	1.3	46.1	0.8	0.2	3.0	8.6	1.1	3.7	1.0	32.6	0.3	210	35.3	0	0.1	2.1	44.5	91.2	100	31.6	2.1	137	-	-	-	-	-	-
GF1	1	389	19.6	0.1	101	2.2	0.4	7.8	13.9	1.8	6.8	1.8	63.5	2.6	341	26.2	2.2	0.1	7.9	79.9	67.3	62.0	78.2	1.4	149	-	-	-	-	-	-
	2	148	5.9	0.1	45.5	0.8	0.3	5.4	10.5	0.7	5.3	1.7	48.7	1.6	299	28.1	1.0	0	2.7	83.1	72.4	73.2	81.1	1.5	146	-	-	-	-	-	-
	3	118	3.7	0.1	37.3	0.6	0.2	5.3	10.4	0.8	4.9	1.6	23.0	2.2	332	35.1	1.0	0	7.2	62.8	67.2	62.7	64.1	1.5	193	-	-	-	-	-	-
	4	98.8	3.6	0.2	33.5	0.8	0.2	5.5	8.8	0.9	4.8	2.0	18.1	0.3	363	36.6	0.1	0.1	3.7	60.9	77.7	76.9	60.0	1.7	154	-	-	-	-	-	-
	5	117	3.6	0.2	40.0	1.1	0.2	6.2	12.6	1.3	4.7	2.8	27.4	1.5	443	41.1	0.3	0.1	7.5	57.2	82.0	78.0	58.1	1.9	213	-	-	-	-	-	-
	6	90.8	4.6	0.4	32.2	1.6	0.3	3.2	10.0	0.8	4.1	2.3	41.1	0.3	420	35.6	0	0.1	2.6	48.8	97.1	82.0	44.9	2.1	150	-	-	-	-	-	-
	7	103	4.2	0.4	36.7	2.0	0.3	3.9	13.2	1.5	4.8	2.6	55.7	1.1	462	41.6	0.2	0.2	4.0	63.3	98.1	85.9	60.4	2.6	169	-	-	-	-	-	-
	8	101	5.3	0.2	35.5	2.4	0.1	3.7	8.9	1.0	3.8	2.6	9.7	0.9	579	47.8	0	0.2	4.8	56.8	85.8	82.8	59.0	2.3	122	-	-	-	-	-	-
	9	97.0	2.7	0.3	46.0	4.9	0.1	2.8	9.7	1.4	2.8	0.9	15.7	1.9	510	48.9	0	0.2	5.9	37.3	89.3	83.3	31.7	1.8	131	-	-	-	-	-	-
	10	96.4	3.1	0.4	42.8	5.4	0.2	2.0	8.9	1.2	2.6	0.6	22.3	0.6	484	46.8	0	0.1	5.1	35.6	92.5	86.9	27.5	1.7	120	-	-	-	-	-	-
	15	70.3	3.3	0.1	26.4	1.1	0.1	2.8	5.4	0.7	3.4	3.1	6.4	0.3	317	37.6	0	0.1	3.1	43.8	98.0	97.7	29.9	2.2	103	-	-	-	-	-	-
	20	47.4	1.3	0	22.6	1.1	0	3.6	4.7	0.3	3.4	1.8	10.4	4.1	133	27.5	1.1	0.1	6.7	73.5	60.9	59.7	72.4	1.4	62.3	-	-	-	-	-	-
	25	48.8	2.7	0.3	19.2	0.9	0.2	3.6	5.3	0.7	3.9	1.6	6.3	0.8	137	24.5	1.0	0.1	2.1	95.2	72.9	75.2	93.5	2.9	127	-	-	-	-	-	-

Table 4d.

		NaCl						NaBD						NaOH						HCl (0.5 M)						HCl (1 M)					
Site	cm	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe
GF2B	1	219	8.4	0.3	56.3	27.4	1.1	16.9	71.8	1.1	17.6	192	43.7	1.5	371	47.3	1.3	2.4	8.9	41.3	96.9	67.7	68.1	199	283	-	-	-	-	-	-
	2	151	5.3	0.4	50.1	12.1	0.7	5.1	10.9	1.0	7.6	25.9	30.7	0	502	53.7	0.3	0.7	3.0	35.5	91.1	81.3	35.9	33.5	244	-	-	-	-	-	-
	3	113	3.7	0.3	41.3	12.1	3.8	1.6	7.0	1.1	2.1	0.8	15.8	0.4	511	59.8	0.1	0.1	4.2	36.5	92.8	89.7	26.0	1.6	143	-	-	-	-	-	-
	4	97.9	2.7	0.2	36.1	9.0	0.2	2.8	6.5	0.7	3.4	2.7	59.5	0.3	518	56.6	0.1	0.2	5.0	35.6	88.5	85.7	28.0	1.8	106	-	-	-	-	-	-
	5	99.4	2.6	0.3	38.3	9.8	1.2	2.6	7.2	0.8	3.5	2.0	71.1	0	579	61.2	0.5	0.1	4.7	40.9	100	90.2	34.6	2.0	132	-	-	-	-	-	-
	6	108	3.5	0.5	39.5	9.5	1.4	3.1	8.1	0.9	3.3	2.6	73.1	0	759	66.4	0	0.2	5.7	39.4	109	92.7	35.5	2.4	145	-	-	-	-	-	-
	7	109	4.0	0.4	42.1	11.2	14.2	2.6	8.2	1.2	2.2	0.8	74.4	0	764	64.7	0	0.2	5.9	39.0	114	93.1	28.9	2.6	147	-	-	-	-	-	-
	8	105	3.0	0.2	39.0	9.5	10.2	2.4	7.9	0.8	2.2	1.2	90.1	0.2	716	55.9	0	0.2	5.2	38.9	113	95.1	28.3	3.4	180	-	-	-	-	-	-
	10	89.3	2.5	0.1	34.6	7.6	0.4	3.1	8.0	0.7	3.3	2.8	71.1	0.1	492	52.6	0.1	0.3	4.2	45.5	101	100	29.5	3.5	125	-	-	-	-	-	-
	13	75.8	2.2	0	31.0	6.9	0.2	2.7	6.4	0.6	3.2	2.3	61.6	0.2	382	48.5	0.1	0.3	3.9	45.5	95.3	93.9	32.0	3.2	132	-	-	-	-	-	-
GF2F	1	274	5.5	0.2	72.9	20.3	0.8	16.7	46.8	0.5	21.8	154	32.6	0.2	321	35.0	0.5	0.8	2.5	40.3	87.0	65.1	80.1	207	274	232	429	606	7.2	27.0	257
	2	147	2.6	0.1	50.6	7.7	0.3	6.9	15.2	0.2	14.5	55.1	27.4	0.1	346	42.9	0.3	0.5	1.9	43.9	101	84.5	67.7	153	315	222	381	595	7.1	7.8	246
	3	141	4.1	0.3	46.2	5.0	0.6	6.1	17.1	0.5	6.1	12.5	31.9	0	558	50.7	0	0.1	2.0	38.5	89.1	85.9	34.5	3.3	192	215	363	570	6.8	2.9	238
	4	127	3.1	0.3	44.4	4.4	0.4	5.0	15.1	0.2	6.4	16.9	30.7	0.1	469	50.1	0	0.2	2.3	40.5	95.3	89.1	38.2	7.8	259	237	385	631	8.4	3.4	266
	5	101	5.5	0.5	36.7	7.3	0.4	2.8	8.7	0.2	3.6	9.3	13.5	0.1	427	47.5	0	0.1	2.0	42.5	91.3	88.7	39.3	3.3	157	218	369	580	7.0	2.9	246
	6	95.5	6.5	0.5	35.1	5.3	0.5	3.4	9.8	0	4.2	10.3	17.8	0.4	453	49.8	0	0.1	2.1	45.0	97.4	93.2	40.4	3.5	159	216	365	590	7.2	2.8	236
	7	96.2	5.6	0.2	35.2	4.5	0.2	3.9	12.4	0	4.9	11.2	29.1	0.1	512	54.0	0	0.1	2.2	45.1	100	95.6	42.8	3.5	191	212	353	578	7.0	2.7	234
	8	98.3	5.3	0.3	37.0	6.3	0.2	3.1	10.5	0	4.5	8.9	21.4	0.1	574	56.9	0	0.1	2.3	49.6	109	102	46.0	3.5	190	209	366	580	6.7	2.7	233
	9	90.9	5.8	0.4	35.1	3.8	0.3	3.5	12.7	0	4.6	9.6	25.3	0	573	56.5	0	0.1	1.8	43.2	98.1	92.0	42.6	2.8	204	196	342	534	6.6	2.5	226
	10	111	7.6	0.5	40.9	4.7	0.3	4.5	15.4	0	5.5	9.7	30.1	0	750	65.2	0	0.2	2.6	45.1	108	98.0	44.2	3.7	184	200	350	522	6.4	2.6	236
	11	113	10.4	0.2	40.1	6.1	0.3	4.3	13.6	0.9	4.8	2.6	18.5	0.2	889	73.9	0.1	0.2	3.8	46.9	124	106	37.4	3.2	160	230	430	645	6.5	2.8	255
	12	119	8.5	0.2	41.7	7.7	0.3	3.4	11.4	0.9	4.2	2.0	17.7	0	903	72.9	0	0.2	4.3	42.9	124	102	35.4	2.9	164	225	402	648	6.7	2.8	249
	13	118	5.1	0.1	41.6	3.9	0.2	6.1	18.8	1.1	6.8	3.0	29.6	0.5	855	70.5	0.3	0.3	11.2	40.4	136	102	34.7	3.4	252	227	426	695	7.9	3.3	246
	14	121	6.3	0.1	42.4	3.1	0.2	6.2	19.9	0.7	6.4	2.8	38.0	0.4	874	72.7	0	0.2	5.3	42.7	141	105	39.5	3.7	293	250	418	740	8.8	3.7	277
	15	120	5.0	0.1	44.1	2.6	0.2	5.8	18.9	0.8	6.0	2.5	32.0	0.8	776	67.5	0.1	0.2	5.7	46.1	141	108	37.7	4.4	349	219	379	630	7.2	3.3	246
	20	69.7	5.4	0	26.3	1.8	0.1	3.9	8.6	0.6	3.7	2.0	15.2	0	339	49.8	0.1	0.2	2.2	49.9	102	95.2	38.1	3.9	157	199	363	538	6.4	2.6	226
	25	67.4	4.8	0.1	25.2	1.3	0.1	4.4	8.1	0.5	3.8	2.0	16.5	0	297	48.6	0	0.2	2.0	49.7	99.0	96.1	34.0	3.9	145	213	363	574	6.3	2.7	239
GF2K	1	284	7.2	0.1	72.7	18.7	0.4	29.9	78.3	5.0	29.5	222	53.0	0	298	38.4	1.0	0.6	1.3	47.6	111	78.5	78.3	191	309	-	-	-	-	-	-
	2	147	3.5	0.1	46.9	6.0	0.3	9.3	17.6	1.3	15.1	52.3	44.8	0	394	46.3	0.8	0.5	1.6	52.5	113	94.7	54.4	74.6	298	-	-	-	-	-	-
	3	122	4.4	0.3	39.8	6.6	0.2	5.3	11.1	1.4	5.6	10	26.5	0	424	53.6	0.2	0.1	1.9	49.3	108	100	37.3	3.7	175	-	-	-	-	-	-
	4	100	4.8	0.1	34.8	4.1	0.2	4.7	11.5	0.8	5.2	9.4	31.8	0	417	53.2	0.4	0.1	1.7	50.7	113	101	39.4	3.3	202	-	-	-	-	-	-
	5	107	4.9	0.1	40	6.0	0.2	3.2	11.6	0.4	4.1	8.3	17.2	2.8	562	71.9	0.8	0.3	10.7	43.5	101	92.9	43.8	3.6	218	-	-	-	-	-	-
	6	111	5.0	0.1	41.1	7.2	0.2	3.0	12.3	0.3	4.0	7.5	23.9	1.4	717	70.4	0.5	0.2	6.0	41.0	101	90.5	39.9	4.0	210	-	-	-	-	-	-
	7	125	7.4	0.5	44.8	6.7	0.4	4.1	16.6	0.3	5.0	10.2	25.8	1.8	853	76.9	0.7	1.1	10.5	44.7	111	94.0	45.3	13.9	222	-	-	-	-	-	-
	8	118	7.8	0.3	42.1	9.2	0.3	3.1	11.5	0.4	3.9	7.5	21.3	0	888	68.7	0.2	0.5	4.5	38.2	106	88.0	35.5	7.1	180	-	-	-	-	-	-
	9	141	8.3	0.2	50.5	7.5	0.4	4.6	15.2	0.4	5.6	7.3	37.4	0.8	1077	80.6	0.4	0.3	13.1	36.3	128	96.3	34.8	3.7	291	-	-	-	-	-	-
	10	125	7.4	0.2	44.2	7.7	0.5	3.2	10.4	0.4	4.0	5.1	20.7	0	896	74.4	0.2	0.2	5.8	33.8	105	88.4	33.0	3.0	159	-	-	-	-	-	-
	13	98.6	5.0	0.1	36.3	8.3	0.2	2.4	9.4	0.5	3.1	5.8	20.1	0.4	668	61.4	0.4	0.3	5.8	39.6	92.0	88.6	34.5	4.6	153	-	-	-	-	-	-
	15	86.9	4.0	0	32.6	6.3	0.1	2.1	7.3	0.1	2.7	4.8	18.0	0	424	56.8	0.2	0.2	2.7	43.1	92.0	94.7	30.8	3.4	168	-	-	-	-	-	-

Table 4e.

Site	cm	NaCl						NaBD						NaOH						HCl (0.5 M)						HCl (1 M)					
		Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe
C63	1	81.7	4.7	0.2	34.2	7.9	0.4	1.7	5.3	0.8	3.6	2.7	26.9	0.2	362	39.0	0	0	3.9	29.1	70.9	62.1	26.5	0.8	68.5	-	-	-	-	-	-
	2	78.4	3.5	0.5	31.2	0.9	0.5	1.5	4.5	0.9	1.7	0.4	15.0	0.2	474	42.3	0	0.1	4.2	29.2	75.1	65.5	23.2	0.7	65.0	-	-	-	-	-	-
	3	90.9	5.7	1.2	35.6	1.4	1.2	1.9	5.1	0.9	2.1	0.5	22.4	0	581	51.1	0	0.1	4.5	36.8	98.6	80.6	22.8	1.2	105	-	-	-	-	-	-
	4	117	8.0	0.3	43.4	1.9	1.5	2.5	8.8	1.1	2.8	0.5	49.3	3.6	1100	72.2	0.2	0.3	16.2	39.1	102	87.9	22.0	1.4	90.8	-	-	-	-	-	-
	5	95.3	5.7	0.3	37.2	1.7	1.6	1.8	6.4	0.8	2.8	0.4	42.1	0	725	51.2	0	0.1	4.0	41.1	99.0	87.6	22.9	1.2	74.2	-	-	-	-	-	-
	6	93.2	5.2	0.3	40.3	2.0	32.0	1.5	8.0	2.4	1.3	0.2	28.0	0	575	50.7	0	0.1	4.5	43.3	106	101	25.6	1.3	98.4	-	-	-	-	-	-
	7	95.4	5.2	0.1	39.7	1.9	29.0	1.3	6.3	0.5	1.7	0.2	33.4	0	629	48.9	0	0.1	3.1	44.0	111	99.9	25.2	1.4	99.8	-	-	-	-	-	-
	8	83.7	4.6	0.1	36.5	1.8	24.4	1.3	5.6	0.7	1.7	0.2	26.2	0	570	46.3	0	0.2	4.9	43.7	110	96.1	25.8	1.4	93.8	-	-	-	-	-	-
	9	62.9	3.3	0.3	31.1	1.6	18.1	0.9	4.6	0.5	0.9	0.1	17.7	1.0	374	41.7	0	0.2	6.4	39.8	91.3	81.2	22.5	1.2	69.0	-	-	-	-	-	-
	10	58.7	3.4	0.2	28.8	1.5	20.2	1.1	4.6	0.7	0.6	0.1	19.4	0.2	334	41.3	0	0.2	3.1	39.2	92.8	79.8	22.9	1.3	75.5	-	-	-	-	-	-
	15	12.7	0.9	1.6	12.3	0.5	2.6	0.4	2.0	0.1	0.4	0.1	4.1	0	32	11.7	0	0	2.0	16.2	36.6	31.7	21.3	0.4	50.3	-	-	-	-	-	-
E3	1	258	7.7	0	74.9	41.9	1.5	5.9	13.3	0.6	6.7	14.2	109	1.8	401	63.6	1.3	0.4	18.2	51.7	107	86.5	43.3	4.8	272	-	-	-	-	-	-
	2	181	4.8	0	57.6	11.4	7.8	4.4	8.0	0.9	4.2	3.1	88.4	1.2	544	56.1	0.2	0.2	13.8	47.3	126	107	31.7	2.2	252	-	-	-	-	-	-
	3	150	5.5	0	50.3	8.3	7.6	4.2	15.5	5.2	3.1	1.6	60.6	1.1	622	58.8	0	0.1	5.1	51.0	130	117	32.7	2.3	186	-	-	-	-	-	-
	4	136	4.6	0	47.9	7.4	5.6	3.0	8.2	1.3	3.2	1.4	64.1	0	603	61.8	0	0.1	2.5	52.0	131	119	34.8	2.4	202	-	-	-	-	-	-
	5	112	3.8	0	38.4	3.8	0.1	6.8	11.6	0.9	6.1	3.9	21.0	0.9	609	59.6	0.2	0.1	5.3	48.9	113	109	41.0	2.9	220	-	-	-	-	-	-
	6	104	4.5	0	36.6	4.0	0.1	7.2	10.9	0.9	6.7	4.5	15.6	1.9	664	67.0	0.5	0.2	8.1	54.4	114	109	47.3	3.0	191	-	-	-	-	-	-
	7	98.0	4.4	0	35.1	4.4	0.1	7.6	11.3	0.9	7.2	5.1	14.3	1.8	665	65.8	0.5	0.2	7.3	58.8	125	115	50.6	3.2	204	-	-	-	-	-	-
	8	107	4.8	0.2	39.0	4.9	0.3	4.7	11.9	0.9	5.1	4.5	23.5	3.4	691	70	0.8	0.2	16.7	47.9	107	101	41.6	2.4	231	-	-	-	-	-	-
	9	111	7.7	0.6	39.1	4.5	0.4	4.5	10.5	1.0	4.4	3.8	16.0	3.3	753	73.0	0.5	0.4	12.8	46.1	113	108	38.0	2.5	134	-	-	-	-	-	-
	10	107	7.7	0.5	37.3	4.4	0.5	4.7	9.8	0.8	4.6	3.6	15.6	1.8	754	70.5	0.1	0.3	9.6	45.0	115	106	35.5	2.5	121	-	-	-	-	-	-
	15	97.4	7.3	0.1	34.0	2.5	0.1	4.7	11.7	0.7	4.0	4.9	15.6	1.3	677	62.7	0.1	0.3	6.5	55.6	126	121	35.9	4.4	183	-	-	-	-	-	-
	20	83.7	6.7	0	29.8	1.9	0	5.7	9.7	0.8	4.3	4.4	12.8	3.1	538	62.8	0.2	0.5	11.0	54.6	119	121	31.0	4.3	150	-	-	-	-	-	-
	25	77.5	5.9	0.1	29.2	1.4	0.1	4.6	7.0	0.2	3.7	4.4	8.2	0.1	298	41.6	0	0.2	1.6	54.0	88.7	98.2	42.5	3.8	113	-	-	-	-	-	-
LL3a	1	155	5.1	0.1	53.9	27.3	0.2	8.7	23.8	1.1	14.1	72.3	135	0	538	55.9	0	0.3	3.2	33.2	89.3	85.6	28.6	7.7	166	-	-	-	-	-	-
	2	117	4.8	0.2	42.4	10.2	0.1	5.2	13.0	1.3	6.1	8.6	81.2	0.8	485	63.2	0	0.1	2.6	35.8	88.3	90.6	28.2	2.0	115	-	-	-	-	-	-
	3	104	4.8	0.2	40.6	10.5	0.2	6.2	12.9	0.9	6.5	11.2	80.6	0.2	478	68.8	0.1	0.1	3.9	35.4	88.7	89.7	28.6	2.2	128	-	-	-	-	-	-
	4	98.4	4.4	0.2	39.6	9.8	0.1	3.9	12.4	1.3	7.7	9.8	69.1	1.5	492	65.2	0.2	0.2	8.7	33.7	86.2	85.9	27.0	1.8	115	-	-	-	-	-	-
	5	98.2	4.0	0.2	39.7	5.1	0.1	5.3	17.6	0.7	6.2	10.1	75.7	0.4	550	68.4	0.1	0.1	3.3	31.4	82.0	84.2	31.4	2.0	161	-	-	-	-	-	-
	6	103	4.1	0.2	40.3	3.5	0	6.6	17.3	0.4	7.6	8.0	72.4	0.3	633	71.8	0	0.1	3.8	30.9	89.7	84.5	29.9	2.3	165	-	-	-	-	-	-
	7	89.4	4.9	0.1	34.1	2.6	0	5.0	13.7	0.8	5.2	5.4	47.1	0.4	555	58.8	0.2	0.1	3.1	32.5	84.5	86.7	28.1	2.6	132	-	-	-	-	-	-
	8	83.2	5.1	0	31.3	2.0	0	5.4	11.7	0.3	4.3	4.7	41.0	0.7	487	54.8	0	0.2	4.1	32.8	84.7	87.1	25.8	3.4	156	-	-	-	-	-	-
	9	80.8	5.6	0.1	30	1.9	0	4.7	10.2	0.6	4.1	4.2	30	0.5	463	48.7	0.2	0.1	2.4	30.8	76.5	81.2	24.4	3.2	119	-	-	-	-	-	-
	10	77.3	5.9	0.2	29.1	1.7	0.1	5.3	10.2	0.3	4.7	4.2	28.1	0.7	467	51.2	0	0.2	3.2	33.8	77.1	85.1	25.6	3.2	110	-	-	-	-	-	-
	15	69.9	4.7	0	26.8	1.1	0	5.6	9.8	0.2	4.9	3.7	29.7	1.3	381	52.1	0.1	0.2	4.1	35.2	73.4	84.0	24.9	2.5	86.5	-	-	-	-	-	-
	20	63.4	3.9	0	24.9	0.7	0	5.0	9.3	0.6	4.0	3.1	36.7	0.8	292	43.1	0	0.1	1.7	36.8	76.3	88.0	28.7	3.1	115	-	-	-	-	-	-
	25	61.5	4.0	0	23.8	0.5	0	5.9	7.9	0.4	4.2	2.5	27.9	0.7	281	44.6	0	0.1	1.7	32.4	69.2	79.4	27.2	2.4	92.2	-	-	-	-	-	-
XVI	1	483	31.2	0.3	129	9.2	0.6	17.0	15.3	0.9	15.9	5.5	64.5	1.2	1390	78.7	0.8	0.3	31.4	24.4	85.2	70.7	21.8	1.6	167	-	-	-	-	-	-
	2	314	16.6	0.5	94.4	6.3	0.9	21.1	37.2	16.3	18.3	8.6	83.6	0.4	1370	87.4	0.3	0.2	14.9	29.6	102	91.9	27.6	2.3	218	-	-	-	-	-	-
	3	202	12.6	0.5	65.8	6.5	0.5	9.3	15.3	0.8	9.6	6.8	58.5	0.8	1325	100	0.5	0.3	18.4	28.7	94.0	88.6	25.4	2.1	172	-	-	-	-	-	-
	4	182	11.7	0.4	61.0	5.8	0.5	8.2	18.5	0.3	8.7	6.6	61.0	1.1	1384	98.3	0.5	0.2	25.5	27.3	95.9	88.6	24.2	1.9	207	-	-	-	-	-	-
	5	195	11.6	0.4	64.7	6.7	0.5	8.9	20.9	0.4	9.6	7.3	73.4	0.5	1509	101	0.3	0.2	13.1	30.2	119	119	27.5	2.4	216	-	-	-	-	-	-
	6	205	7.8	0.4	72.9	13.6	13.6	5.5	14.2	0.7	5.5	2.2	66.6	0.8	1414	104	0.3	0.2	20.3	32.6	120	114	28.9	2.0	192	-	-	-	-	-	-
	7	216	9.1	0.2	81.8	16.5	16.7	6.1	15.3	0.7	13.7	3.3	66.6	0.9	1434	105	0.6	0.2	18.5	29.6	99.7	96.9	27.3	1.8	162	-	-	-	-	-	-
	8	206	8.6	0.2	73.3	17.2	4.7	7.7	17.9	0.9	8.1	4.2	74.3	0	1468	101	0	0.1	5.5	29.7	103	104	26.1	1.9	155	-	-	-	-	-	-
	9	165	18.0	9.2	74.2	16.4	62.1	1.9	19.9	1.2	3.0	0.5	163	0	1273	99.2	0.4	0.1	3.8	35.3	99.5	102	18.4	1.3	101	-	-	-	-	-	-
	10	145	17.2	14.6	70	17.2	54.0	0.9	18.5	0.9	0.7	0.3	163	0	1156	101	0.1	0.1	4.2	37.9	97.8	99.8	18.6	1.5	116	-	-	-	-	-	-
	15	141	5.9	0.3	55.6	11.9	1.0	4.9	13.5	0.5	6.3	4.4	61.5	0	1025	82.6	0.7	0.2	3.5	30.8	99.3	107	26.2	2.4	178	-	-	-	-	-	-

Table 4f.

		NaCl						NaBD						NaOH						HCl (0.5 M)						HCl (1 M)					
Site	cm	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe	Mg	Si	Al	Ca	Mn	Fe
AS2	1	-	7.2	0	50.3	2.6	0	-	8.8	1.0	8.6	6.5	63.2	-	562	64.7	0.2	0.2	11.5	-	91.1	101	21.2	1.4	93.7	265	460	594	7.0	2.8	268
	2	-	4.1	0	52.2	2.4	0	-	6.2	1.1	5.0	0.9	45.9	-	555	63.0	0	0.1	4.0	-	107	118	24.0	1.2	87.9	243	399	550	7.8	2.5	239
	3	-	3.1	0	64.1	2.0	0	-	8.2	1.5	7.3	2.4	66.3	-	528	70.2	0	0.1	6.9	-	109	128	24.8	1.4	163	251	354	545	8.8	2.6	268
	4	-	3.4	0	58.7	3.0	0	-	8.0	1.0	6.9	3.0	71.3	-	517	74.6	0.1	0.2	13.9	-	106	120	23.1	1.5	144	247	384	556	9.6	2.6	254
	5	96.0	5.9	0.1	59.6	1.9	0.1	6.2	10.2	0.8	10.9	5.1	24.7	0.2	434	54.5	0.2	0.1	2.4	39.1	93.9	135	24.0	2.6	170	291	375	690	6.0	3.3	321
	6	96.5	4.9	0.1	51.5	2.4	0	6.6	9.5	0.7	11.1	5.6	25.6	0	433	54.5	0	0.1	2.2	36.6	87.8	133	22.1	.7	140	293	392	694	6.3	3.3	323
	7	93.2	6.2	0.2	47.2	2.2	0.1	7.5	8.7	0.9	12.1	5.8	20.2	0	430	53.2	0.2	0.1	1.9	37.6	86.5	141	23.8	2.9	118	279	380	691	6.9	3.2	295
	8	94.4	5.5	0.2	48.5	2.6	0.1	5.6	9.0	0.5	9.5	5.5	29.6	0.6	445	57.5	0	0.1	3.0	38.0	90.5	133	25.2	1.8	158	262	367	656	6.5	3.0	281
	9	99.2	5.3	0.1	49.3	2.5	0.1	5.8	11.6	0.3	9.4	5.4	20.4	0.4	492	61.1	0	0.1	1.7	46.9	98.9	128	28.5	2.3	201	268	380	635	7.1	3.1	310
	10	98.2	4.0	0.2	49.8	5.1	0.3	3.0	8.8	0.2	6.2	3.1	23.1	0.9	468	61.5	0	0.1	3.9	48.3	96.7	129	26.0	2.2	194	249	361	599	7.2	2.8	271
	15	101	3.9	0.1	47.5	2.0	0.1	6.0	10.8	0.4	9.1	4.1	19.3	1.6	297	59.1	0	0.1	4.9	44.2	102	120	26.0	2.2	187	308	433	704	8.4	3.8	362
	20	96.6	4.0	0	46.3	1.2	0	6.8	9.9	0.8	10.1	3.8	14.5	1.0	221	54.2	0	0.2	3.7	42.8	94.5	116	25.4	2.6	148	312	428	717	8.7	4.1	366
	25	94.3	4.2	0	43.0	1.1	0	6.9	8.4	0.5	9.4	3.3	12.5	1.2	244	55.6	0	0.2	3.5	46.3	100	124	26.1	2.6	141	316	417	705	8.4	4.1	369
BISA1	1	507	39.8	0.1	149	77.8	0.2	14.9	13.9	1.6	13.8	14.5	39.4	0.1	1094	60.2	0.2	0	6.2	18.8	55.5	43.7	13.0	1.4	75.6	-	-	-	-	-	-
	2	232	18.4	0.5	77.9	9.3	0.4	9.7	16.6	1.6	12.0	8.0	59.9	0.4	1083	77.0	0.3	0.1	7.9	27.5	83.3	75.8	21.7	1.6	183	-	-	-	-	-	-
	3	325	21.1	0.3	107	9.4	0.5	23.8	28.9	1.3	22.7	12.2	129	0.3	1542	90.7	0.4	0	9.8	38.3	141	128	36.5	3.3	248	-	-	-	-	-	-
	4	158	14.0	0.4	58.7	6.6	0.3	6.9	17.8	1.5	8.8	7.4	69.2	0.3	1141	88.4	0.5	0.2	13.8	30.7	90.5	90.5	23.8	1.9	133	-	-	-	-	-	-
	5	135	10.9	0.4	53.4	5.9	0.3	7.1	17.2	1.6	8.9	7.1	62.2	0	1031	85.2	0.3	0.1	3.7	31.0	91.5	94.4	23.8	1.9	148	-	-	-	-	-	-
	6	130	10.1	0.4	53.7	5.9	0.1	6.4	21.7	3.1	8.6	7.1	77.4	0.1	1038	88.7	0.3	0.1	6.1	32.3	97.7	97.1	23.9	1.7	173	-	-	-	-	-	-
	7	116	5.6	0.6	48.6	5.4	0.3	8.6	29.6	5.7	9.0	6.2	46.6	1.3	944	83.9	0.3	0.1	15.7	27.1	93.4	87.6	22.7	1.8	251	-	-	-	-	-	-
	8	138	9.2	0.3	55.6	5.4	0.3	10.0	21.4	1.3	11.2	8.1	43.6	2.0	1152	95.8	0.5	0.2	20.9	29.9	104	101	23.2	2.3	265	-	-	-	-	-	-
	9	137	9.1	0.5	54.1	5.5	0.3	10.1	20.8	0.7	11.2	7.8	60.6	2.8	1245	98.9	0.4	0.2	24.0	31.5	109	105	22.4	2.2	247	-	-	-	-	-	-
	10	158	12.1	0.4	60.4	6.8	0.3	9.5	21.2	0.5	10.4	7.6	73.4	2.5	1394	101	0.6	0.3	28.4	32.6	107	106	23.0	2.3	204	-	-	-	-	-	-
	15	110	9.0	0.8	49.2	6.7	0.4	5.6	11.6	1.1	8.1	9.7	32.1	1.5	907	106	0.1	0.2	10.3	34.0	94.7	94.5	25.8	2.8	184	-	-	-	-	-	-
	20	87.7	5.3	0.4	41.4	6.2	0.1	4.9	9.6	0.7	7.9	11.2	34.5	1.1	659	94.6	0.1	0.3	8.4	31.7	87.0	91.3	25.5	3.7	203	-	-	-	-	-	-
	25	57.6	3.7	0.3	27.8	4.9	0.1	2.7	5.9	0.4	4.4	6.5	28.2	1.8	412	66.7	0.2	0.2	9.1	25.0	62.7	63.5	23.1	1.8	116	-	-	-	-	-	-
BZ1	1	430	24.6	0.6	133	21.1	0.9	20.1	15.6	1.4	19.0	12.0	91.1	2.2	1506	106	0.8	0.4	29.1	28.6	90.2	84.9	23.4	2.0	143	153	438	542	7.1	1.8	131
	2	209	10.8	0.2	71.5	12.2	0.3	8.6	17.7	1.3	10.5	8.6	85.0	0.8	1278	98.1	0.2	0.2	17.4	26.8	88.8	78.4	22.9	1.9	200	158	390	549	5.9	2.0	164
	3	187	10.1	0.4	67.4	10.3	0.4	9.0	19.2	0.9	7.6	12.6	105	0.9	1321	101	0.7	0.2	13.4	30.6	102	91.6	25.2	2.7	246	182	376	626	5.5	2.3	201
	4	155	7.3	0.3	59.3	9.7	0.3	8.2	14.5	2.0	12.0	11.4	56.4	1.0	1185	99.8	0.3	0.3	15.0	29.3	89.6	83.2	24.3	2.9	191	170	391	604	5.4	2.3	184
	5	166	6.9	0	65.6	16.1	0.3	6.3	15.0	1.1	9.6	9.1	50.5	2.7	1372	106	1.1	0.5	36.1	28.3	95.7	84.0	23.7	2.6	189	173	429	618	5.5	2.3	178
	6	154	9.6	0.2	59.1	9.0	0.2	7.4	14.4	1.1	9.6	8.8	45.2	0.7	1296	104	0.2	0.2	10.7	29.1	89.1	86.1	24.3	2.4	158	170	415	612	5.4	2.2	181
	7	160	7.5	0	62.8	7.4	0.1	8.9	17.5	0.9	11.3	9.3	92.0	0.8	1420	114	0.3	0.2	13.4	30.3	103	93.9	25.6	2.8	259	184	394	680	5.5	2.4	193
	8	133	7.4	0.1	52.7	7.6	0.2	7.2	12.6	1.0	9.1	8.6	54.0	0	1228	103	0	0.1	2.7	31.7	101	97.9	27.0	3.3	221	195	354	683	4.8	2.4	219
	9	124	6.8	0	51.0	6.6	0.2	6.7	12.9	1.3	9.1	9.2	51.3	0.1	1136	105	0	0.2	4.0	34.2	106	102	27.5	4.0	262	207	379	736	5.0	2.6	234
	10	118	6.3	0	49.5	7.6	0.1	5.1	10.8	1.3	6.9	7.2	39.2	0	1057	95.9	0	0.1	2.5	35.0	115	107	27.7	4.7	276	212	359	717	4.9	2.7	253
	15	119	7.7	1.0	49.7	8.4	0.2	4.3	9.8	1.1	6.3	6.5	35.2	0.4	1204	105	0.1	0.2	5.6	35.2	107	107	27.6	3.6	213	209	372	679	4.7	2.8	248
	20	113	8.3	0	47.3	6.6	0.1	5.1	10.9	2.4	6.5	5.3	38.0	0	1213	97.1	0	0.2	4.0	34.6	111	108	24.5	3.2	213	210	365	664	4.4	3.1	259
	25	107	9.7	0	45.0	4.9	0.1	4.8	11.0	1.2	6.8	6.1	31.9	0	1148	93.9	0	0.2	4.6	35.1	107	103	24.0	2.9	196	199	365	660	4.6	3.0	239